



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: B22F 9/12	A1	(11) International Publication Number: WO 98/09753 (43) International Publication Date: 12 March 1998 (12.03.98)
(21) International Application Number: PCT/US97/15463 (22) International Filing Date: 3 September 1997 (03.09.97) (30) Priority Data: 08/706,819 3 September 1996 (03.09.96) US 08/707,341 3 September 1996 (03.09.96) US (71) Applicant: NANOMATERIALS RESEARCH CORPORATION [US/US]; 2849 East Elvira Road, Tucson, AZ 85706 (US). (72) Inventors: PIRZADA, Shahid; 6960 N. Avenida Adella, Tucson, AZ 85741 (US). YADAV, Tapesh; 5238 E. Mission Hills, Tucson, AZ 85718 (US). (74) Agent: PASTERNAK, Sam; Choate, Hall & Stewart, Exchange Place, 53 State Street, Boston, MA 02109 (US).		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: INTEGRATED THERMAL PROCESS AND APPARATUS FOR THE CONTINUOUS SYNTHESIS OF NANOSCALE POWDERS <div data-bbox="451 1117 1117 1564" data-label="Diagram"> </div>		
(57) Abstract <p>A continuous process that produces nanoscale powders from different types of precursor material by evaporating the material and quenching the vaporized phase preferably in a converging diverging expansion nozzle. The precursor material suspended in a carrier gas is continuously vaporized at very high temperatures, preferably exceeding 2000 degrees C, and most preferably exceeding 5000 degrees K, in a thermal reaction chamber under conditions that favor nucleation of the resulting vapor. Immediately after the initial nucleation stages, the vapor stream is rapidly and uniformly quenched at rates of at least 1,000 K/sec, preferably above 1,000,000 K/sec, to block the continued growth of the nucleated particles and produce a nanosize powder suspension of narrow particle size distribution. The nanopowder is then harvested by filtration from the quenched vapor stream and the carrier medium is purified, compressed and recycled for mixing with new precursor material in the feed stream.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

INTEGRATED THERMAL PROCESS AND APPARATUS FOR THE CONTINUOUS SYNTHESIS OF NANOSCALE POWDERS

BACKGROUND OF THE INVENTION

5

This invention pertains in general to a process and apparatus for the synthesis of submicron particles. In particular, the invention relates to a novel approach utilizing vaporization and ultra-rapid thermal quenching based on adiabatic expansion of the vapor through a boundary layer converging-diverging nozzle to produce
10 submicron particles under controlled operating conditions.

As defined in the art, submicron powders are materials having average grain size below 1 micrometer. Of particular interest are nanoscale powders; namely, submicron powders with grain size less than 100 nanometers and with a significant fraction of interfacial atoms. Of great interest are powders with grain size of less than
15 50 nanometers. Of greater interest are powders with grain size less than 20 nanometers. Of greatest interest are powders with grain size less than 10 nanometers. It is known that within these size ranges a variety of confinement effects occur that dramatically change the properties of the material. A property will be altered when the entity or mechanism responsible for that property is confined within a space
20 smaller than some critical length associated with that entity or mechanism. See H. Gleiter, Mechanical Properties and Deformation Behavior of Materials Having Ultra-Fine Microstructures, Nastasi et al. Ed., 3-35 (1993); and R. W. Siegel, Mechanical Properties and Deformation Behavior of Materials Having Ultra-fine Microstructures, Nastasi et al. Ed., 509 (1993), which are included herein by reference. Such
25 confinement effects can, therefore lead to a wide range of commercially important properties. For example, a normally ductile metal will become significantly harder if its grain size is reduced to the point where moving dislocations through its crystal lattice are no longer able to occur at normal levels of applied stress. Since the stress required to produce a Frank-Read dislocation is inversely proportional to the spacing
30 between its pinning points, as one skilled in the art would readily understand, a critical length in this case is that for which the stress necessary to produce a dislocation becomes larger than the conventional yield stress for the given metal.

Thus, confinement effects can be exploited to produce extremely hard and strong materials with much higher yield stress than exhibited by the conventional form of their precursors. See Nieman et al., "Mechanical Behavior of Nanocrystalline Cu and Pd," J. Mater. Res., 6, 1012 (1991); and Nieman et al., "Tensile Strength and Creep Properties of Nanocrystalline Palladium," Scripta Metall. et Mater., 24, 145 (1990), which are included herein by reference. The same principle has also been used to manufacture unique optical materials with grain sizes tailored for excitonic interactions with particular wavelengths, Skandon et al., "Nanostructured Y_2O_3 : Synthesis and Relation to Microstructure and Properties," Scripta Metall. et Mater., 25, 2389 (1991); electroceramics with unique electronic and electrical characteristics, Eastman et al., "Processing and Properties of Nanophase Oxides," Mater. Res. Soc. Symp. Proc., 155, 255 (1989); superplastic ceramics with grain sizes engineered to allow low cost, rapid net-shape forming of ceramics as a substitute process for machining of ceramics. H. Hahn et al., "Low Temperature Sintering and Deformation of Nanocrystalline TiO_2 ," Mater. Res. Soc. Symp. Proc., 196, 71 (1990) and M. J. Mayo, Mechanical Properties and Deformation Behavior of Materials Having Ultra-fine Microstructures, Nastasi et al. Ed., 361 (1993); catalysts with extremely high surface areas, high selectivity and activity, Beck and Siegel, "The Dissociative Adsorption of Hydrogen Sulfide over Nanophase Titanium Dioxide," J. Mater. Res., 7, 2840 (1992); materials with unique electrochemical properties, Tamaki et al., "Grain-Size Effects in Tungsten Oxide-Based Sensor for Nitrogen Oxides," J. Electrochem. Soc., 141, 2207 (1994); and materials that exhibit unprecedented magnetic properties, Sugaya et al., "Soft Magnetic Properties of Nanostructure-Controlled Magnetic Materials," IEEE Trans. on Magnetics, 31, 2197 (1995) and C.E. Yeack-Scranton, Nanomagnetism, Kluwer Academic, Netherland, 1-6 (1993), all of which are included herein by reference. Quantum confined and nanometer cluster materials, therefore, are an extraordinary opportunity for design, development and commercialization of a wide range of structural, electrochemical, electrical, optical, electronic, magnetic and chemical applications. Furthermore, since they represent a whole new family of material precursors where conventional coarse-grain physiochemical mechanisms are not applicable, these materials offer a unique

combination of properties that can enable novel and multifunctional components of unmatched performance.

Although this opportunity has been apparent for several years, large scale commercialization has remained unrealized because of the high cost and low
5 throughput of existing processes for producing nanopowders, the current lack of process control over size and size distribution of the resulting material, the unpredictable composition of its constituent phases, and the lack of control over the nature of and the interactions among the interfaces created between the constituent phases. Nanopowders may indeed represent the threshold of a new era in materials
10 technology, but the key to their full utilization depends on the development of new processes for producing nanopowders economically and in commercially viable quantities under controlled operating conditions.

In recent years, several methods have been used for producing nanopowders and the materials produced by this prior-art technology have confirmed the fact that
15 nanopowders possess important technical properties that show the potential for becoming commercially significant. However, all known production methods consist of batch processes that are too expensive to yield commercially affordable materials for bulk applications (current production costs for these processes are orders of magnitude higher than the \$10.00/lb target price considered economical for bulk
20 applications of these materials). Therefore, the commercial future of nanopowders depends on the development of a process that can produce nanopowders with predetermined properties, in commercially viable quantities, and at an affordable cost.

An additional and significant problem encountered by the performance ceramics industry is the use of environmentally undesirable solvents and additives
25 (acids, alkalis, ammonia and aromatic dispersants to name a few examples) in large quantities. Unfortunately, the present processing techniques continue to require the use of solvents and additives and the anticipated growth in this market for ceramic devices suggests that this environmental hazard will only increase.

Ideally, the synthesis and processing technology for nanopowders should
30 allow control of the size and size distribution of the constituent structures and phases (this is critical to the mechanistic performance of nanopowders); allow control of the composition of the phases in the nanomaterial (critical to define the property domain

of the nanomaterial); allow control over the nature of interfaces (e.g. purity) and the interaction between interfaces (critical to the interface-based characteristics of the nanopowders); and minimize the use of environmentally undesirable solvents and additives. None of the known processes for the synthesis of nanomaterials possesses these characteristics; therefore, none is suitable for bulk commercialization of nanopowders.

In particular, prior-art processes are all batch, and have high energy or solvent processing requirements, which are all inherent limitations to the cost-effective and large-scale production of nanopowders. The processes currently in use can be classified into three general groups: chemical, mechanical-attrition, and gas-condensation methods. The chemical methods include precipitation techniques, sol-gel processes, and inverse-micelle methods. See Beck and Siegel, "The Dissociative Adsorption of Hydrogen Sulfide over Nanophase Titanium Dioxide," J. Mater. Res., 7, 2840 (1992), and Steigerwald and Brus, "Synthesis, Stabilization, and Electronic Structure of Quantum Semiconductor Nanoclusters," 11 Ann. Rev. Mater. Sci., 191 471 (1989), which are included herein by reference. These processes have been used to successfully synthesize narrowly distributed nanopowders; however, being chemical-media based, the resulting nanopowders are covered with chemical surface layers. This surface covering adversely affects the properties of the nanopowders and inhibits their further processing into bulk materials. In addition, the use of solvents and chemicals has a significant economic impact on the synthesis process because of the costs of chemicals and, as discussed above, the pollution remediation required by their use.

The mechanical attrition methods rely on the physical decomposition of coarser grains through severe mechanical deformation. Such processing methods are energy intensive, have low flexibility, are susceptible to contamination by attrition tools or media, and afford little control over the quality and consistency of the final product.

The gas condensation methods essentially involve the evaporation of a coarse (at least micron size) source of precursor material, such as a metal, inorganic, etc., in an inert gas at a low pressure. The evaporated source atoms or molecules collide with the gas atoms or molecules and lose energy, thereby causing a homogeneous

condensation of atom or molecule clusters in the supersaturated vicinity of the precursor source. The further accretion and/or coalescence of the nucleated particles is minimized by rapid removal of the nanometer-sized powders so formed from the region of supersaturation. See R. Uyeda, "Studies of Ultrafine Particles in Japan: Crystallography, Methods of Preparation and Technological Applications," 11 Prog. Mater. Sci., 35, 1 (1991), and R. W. Siegel, Materials Science and Technology, 15, VCH, Weinheim, 583 (1991), which are incorporated herein by reference.

Alternatively, gas condensation processes may involve gas-phase reactions. Some of the known gas condensation processes have produced nanomaterials of acceptable size distribution, but they are all batch operations and are not readily scaleable for commercial exploitation.

Additionally, rapid solidification processing of high temperature liquids and vapors has been extensively researched. See Loren A. Jacobson and J. McKittrick, "Rapid Solidification Processing", Materials Sciences & Eng., R-11, 355-408 (1994), which is incorporated herein by reference. Such process techniques are used to prepare fine microstructures (micron sized), increase solid solubility of alloy elements, and prepare non-equilibrium phases, particularly in powder metallurgy. Conventional rapid solidification methods, such as oil quench, gas quench, chill casting, and centrifugal atomization, achieve thermal quench rates of 10^2 to 10^5 K/sec.

Higher quench rates are very desirable because they can enable the synthesis of powders that are submicron in domain size and, at rates greater than 10^6 K/sec, can enable the synthesis of powders with domain size less than 100 nanometers. As defined in the art, submicron powders are materials having average grain size below 1 micrometer. Of particular interest are nanoscale powders; namely, submicron powders with grain size less than 100 nanometers. Finer domain sizes are desirable because the physiochemical properties of materials are remarkably different and commercially useful when the domain size is reduced below 100 nanometers. Nanoscale powders also exhibit very high surface areas and enhanced surface activity for physical and chemical reactions.

To achieve higher cooling rates, contact quenching methods such as splat cooling and glazing have been suggested. See Jones, "Splat Cooling and Metastable

Phases," Rep. Progr. Phys., 36, 1425 (1973), which is incorporated herein by reference. However, these methods are not suitable for thermal quenching of high temperature vapors (greater than 1500 K) because these temperatures lead to thermokinetic transformations from reactions at contact surfaces. These methods are also not useful for high temperature vapors of materials such as carbides, nitride, refractory metals, alloys, and multiphase nonequilibrium phases because the high temperatures can irreversibly damage the contact surfaces. Furthermore, these prior-art methods are not suited for thermally quenching high temperature, chemically-active vapors (such as those resulting from chemical reactions between feed components at high temperatures).

U. S. Patents 5,407,458, 5,403,375, 5,384,306, and 5,389,585 by König et al. all describe the production of nanoscale powders using a process of the reaction of chemically active vapors between feed components at high temperatures. The corresponding metal compounds and corresponding reactants are reacted in the gas phase in a reactor at a temperature of 2000 degrees C or lower, homogeneously condensed directly from the gas phase in the absence of any wall reactions and subsequently removed from the reaction medium. It is asserted that, by separately preheating the process gases to at least the reaction temperature, the nucleation site can be confined. A flow optimized hot wall reactor is used as the source because it is believed by König et al that other sources such as a plasma flame or laser beam result in uncontrollable reaction conditions prevailing in various parts of the reaction zone with very steep temperature gradients and/or turbulent flow conditions, resulting in the powders having broad particle size distribution. The nozzle in the König et al. process relates to feed system of the process and does not mechanistically participate with the evaporation, reactions, condensation or growth of fine powders. Most notably, because the process described by König et al. is a reactive process, byproducts such as HCl are formed, which ultimately affect the purity of the nanomaterials. Because their temperature is limited to 2000 degrees, the process is limited to precursors that have a vaporization temperature less than 2000 degrees C. In addition, König et al. teach a laminar flow technique that would face scale up limitations. This is so because the powder characteristics are related to residence time of gases in the reactor, which in turn is related to the parabolic flow associated with

laminar flow. In other words, in the König et al. process, there is a radially varying profile in residence time (the gas at the center is moving faster than the gas near the wall). As the reactor is scaled up, the powder size will get more broad in distribution.

5 Therefore, there continues to be a need for a low-cost process (less than \$10/lb) that is suitable for large-scale production of nanopowders under controlled operating conditions. The present invention discloses a pioneering and unique thermal condensation process. This process can be a strictly physical process which starts with a material, vaporizes it at very high temperatures (above 2000 degrees C),
10 then very rapidly recondenses it to produce nanoscale powders, thus eliminating the formation of undesirable byproducts. This process satisfies these requirements for the continuous production of nanopowders in bulk quantities, and additionally discloses a Joule-Thompson nozzle that is particularly suited for ultra-rapid quenching and condensation of vaporized material described above.

15

SUMMARY OF THE INVENTION

One of the objectives of this invention is a low capital-cost process for the production of quantum confined and nanometer cluster materials of various inorganic
20 compositions including but not limited to carbides, nitrides, oxides, chalcogenides, halogenides, alloys, metals, complex compositions, and composites in bulk quantities.

Another objective of this invention is to develop techniques to control the size, shape,
25 surface area, morphology, surface characteristics, surface composition, distribution, and degree of agglomeration.

Another objective of the invention is a device that enables very high quench rates of high temperature vapors that can produce nanoscale powders.

30

Yet another objective of this invention is to develop a method of preventing the deposition of the quantum confined and nanometer cluster materials on the walls of the process equipment.

- 5 Another objective is to develop a process which allows vaporization of ingredients at very high temperatures (> 2000 degrees C) yet permits quenching at very high rates.

Yet another objective is to develop a process which produces product but generates no byproduct.

10

A further objective of this invention is to develop a method of ensuring high yield and high selectivity, including but not limited to harvesting 95% + of the quantum confined and nanometer cluster material produced.

- 15 Yet another objective of this invention is to prevent the damage of the quantum confined and nanometer cluster materials during and after their synthesis.

Another objective is a device that is simple, easy to operate, and flexible with respect to operating parameters, so as to allow the production of multiple products.

20

Another objective is a device that prevents contamination of the quenched product from the materials of construction used for the quench equipment.

- 25 Yet another objective is a device that allows flexibility in the composition of the vapor quenched, in quench rates and quench volume.

Another objective of the invention is a process and device that can be carried out with low utility costs (that is, low energy input, energy output, and maintenance expenses).

- 30 Another objective is a process and device with low operating costs (i.e., labor, recycling, raw materials, plant space, etc.); accordingly, the invention aims at a process and device with high yield per pass and high product selectivity.

Another objective is a process that is continuous and suitable for scaling up to production rates in the order of tons per day.

Yet another objective is a process that is simple, easy to operate, and flexible, so as to
5 allow the production of multiple products with relatively simple operating changes.

Still another objective is a process and device that are safe and environmentally benign.

10 Finally, another objective is an operationally stable process that requires a minimal external-control structure for steady-state operation.

A process that satisfies most of these features would be very desirable because it would enable the economical manufacture of nanopowders in bulk quantities.

15 Therefore, according to the foregoing objectives, one aspect of the this invention involves the continuous vaporization at very high temperatures of commercially-available, coarse precursor material suspended in a carrier gas in a thermal reaction chamber under conditions that minimize superheating and favor nucleation of the resulting vapor. Optionally, a kinetic gas feed may be mixed with the vapor in the
20 reactor to reach a thermokinetic state of the vapor that may be required to produce controlled nucleation of solid powders from the vapor stream. Immediately after the initial nucleation stages, the vapor stream is rapidly and uniformly quenched at rates of at least 1,000 K per second, preferably greater than 1,000,000 K per second, to block the continued growth of the nucleated particles and produce a nanosize powder
25 suspension of narrow particle-size distribution. The nanopowder is then harvested by filtration from the quenched vapor stream and the carrier medium is purified, compressed and recycled for mixing with new precursor material in the feed stream.

According to another aspect of the invention, the thermal quenching is carried out in a converging-diverging expansion nozzle that exploits the Joule-Thompson
30 principle of adiabatic expansion of high-temperature vapors. Since the physical characteristics of the nozzle determine the extent of cooling, pressure drop and density drop, the condensation process can be advantageously controlled by utilizing

a nozzle of predetermined key dimensions to fit the requirements of the material being condensed.

Various other purposes and advantages of the invention will become clear from its description in the specification that follows and from the novel features particularly pointed out in the appended claims. Therefore, to the accomplishment of
5 the objectives described above, this invention consists of the features hereinafter illustrated in the drawings, fully described in the detailed description of the preferred embodiments and particularly pointed out in the claims. However, such drawings and description disclose only some of the various ways in which the invention may be
10 practiced.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic representation of the adiabatic-expansion, thermal quenching process of the present invention.

5

Figure 2a is a sketch of a converging-diverging nozzle illustrating the relationship between critical parameters of the process and of the nozzle used to carry out the invention.

10 Figure 2b is a sketch of a converging-diverging nozzle illustrating the key design parameters of the device.

Figure 3a, 3b and 3c are cross-sectional elevational, top, and cross-sectional elevational drawings, respectively of a converging-diverging, adiabatic expansion
15 nozzle according to the preferred embodiment of the invention.

Figure 4 is a schematic illustration of a pilot-plant process according to the preferred embodiment of the invention.

20 Figures 5a, 5b, 5c, and 5d are drawings of the preferred embodiment of the present invention for a scaled up process.

Figure 6 is the transmission electron micrograph of the zinc nanosize powder produced by the invention.

25

Figure 7 is an X-ray diffraction patterns of the product of Example 1, indicating that the only phase present was zinc.

Figure 8 is a SEM micrograph of the feed powders iron and titanium used, showing
30 that they were greater than 1 micrometer when fed.

Figure 9 is a transmission electron microscope image of the iron-titanium alloy nanopowders produced in Example 2, showing them to be in the 10-45 nanometer range.

- 5 Figure 10 is an X-ray diffraction pattern of the product of Example 2, indicating that the phases formed were titanium, iron and iron-titanium intermetallic.

Figure 11 is a transmission electron microscope image of the nickel aluminide nanopowder produced in Example 3.

10

Figure 12 is an X-ray diffraction pattern of the product of Example 3, indicating that the phase formed was NiAl.

- 15 Figure 13 is a transmission electron microscope image of the tungsten oxide nanopowder produced in Example 4.

Figure 14 is an X-ray diffraction pattern of the product of Example 4, indicating that the phase formed was WO_3 .

- 20 Figure 15 is a transmission electron microscope image of the cerium oxide nanopowder produced in Example 5.

Figure 16 is an X-ray diffraction pattern of the product of Example 5, indicating that the phase formed was CeO_2 .

25

Figure 17 is a transmission electron microscope image of the silicon carbide nanopowder produced in Example 6.

- 30 Figure 18 is an X-ray diffraction pattern of the product of Example 6, indicating that the phase formed was SiC.

Figure 19 is a transmission electron microscope image of the molybdenum nitride nanopowder produced in Example 7.

Figure 20 is an X-ray diffraction pattern of the product of Example 7, indicating that
5 the phase formed was Mo_2N .

Figure 21 is a scanning electron microscope image of the nickel boride ceramic used in Example 8, showing that the feed powder was greater than 1 micrometer.

10 Figure 22 is a transmission electron microscope image of the Ni and Ni_3B nanopowders produced in Example 8, showing them to be in the 10-30 nanometer range.

Figure 23 is an X-ray diffraction pattern of the product of Example 8, indicating that
15 the phases formed were Ni and Ni_3B .

Figure 24 is a transmission electron microscope image of the calcium-oxide nanopowders produced in Example 9, showing them to be in the 5-20 nanometer range.

20

Figure 25 is an X-ray diffraction pattern of the product of Example 9, indicating that the phase formed was CaO.

Figures 26a and 26b are transmission electron microscope micrographs of barium
25 titanate produced in Example 10.

Figure 27 is an X-ray diffraction pattern of barium titanate produced in Example 10.

Figures 28a and 28b are transmission electron microscope micrographs of strontium
30 titanate produced in Example 10.

Figure 29 is an X-ray diffraction pattern of strontium titanate produced in Example 10.

Figures 30a and 30b are transmission electron microscope micrographs of barium
5 titanate produced in Example 10.

Figure 31 is an X-ray diffraction pattern of barium titanate produced in Example 10.

Figure 32 is a transmission electron microscope micrograph of nickel zinc ferrite
10 produced in Example 11.

Figure 33 is an X-ray diffraction pattern of nickel zinc ferrite produced in Example 11.

Figures 34a and 34b are transmission electron microscope micrographs of Ni/Cr/Co/Mo alloy
15 produced in Example 12.

Figure 35 is an X-ray diffraction pattern of Ni/Cr/Co/Mo alloy produced in Example 12.

Figure 36 is a transmission electron micrograph of bismuth telluride produced in
20 Example 13.

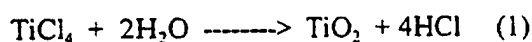
Figure 37 is an X-ray diffraction pattern of bismuth telluride produced in Example 13.
25

DETAILED DESCRIPTION OF THE INVENTION

A primary aspect of this invention lies in the discovery that the size and size distribution of nanopowders produced by vapor condensation can be controlled by
5 interrupting the growth process through ultra-rapid thermal quenching of the condensing vapor. Another critical aspect of the invention is the realization that Joule-Thompson adiabatic expansion provides a controllable process for quenching such condensing vapor at predetermined rates as high as 10^6 °C/sec, or greater, as required for producing nanopowders of desired properties. A third, important aspect
10 of the invention is the development of a converging-diverging nozzle to implement the adiabatic expansion process of the invention under predictable conditions for a variety of precursor materials and operating conditions.

Referring to the drawings, wherein like parts are designated throughout with like numerals and symbols, Fig. 1 shows the process flow diagram and a schematic
15 representation of the apparatus of the invention as applied to solid precursors, such as metals, alloys, ceramics, composites, and combinations thereof. It is understood that the process applies equivalently to other forms of precursors such as liquid, gaseous, slurry, and combinations thereof. A feed stream 10 of such a precursor material in powder form is premixed with a feed gas stream 12 (such as argon, helium, nitrogen,
20 oxygen, hydrogen, water vapor, methane, air, or a combination thereof, depending on the particular precursor being processed and the corresponding atmosphere - inert, oxidizing, or reducing - required for the process) in mixing apparatus 14 appropriate to create a suspension. It is preferred that the feed be a low-cost, coarser form of composition desired. However, if the coarse form is expensive, it is equally feasible
25 to use a mix of low-cost precursors that when combined reflect the composition desired. While stoichiometry is preferred, non-stoichiometric feed ratios can be used if the non-stoichiometric feed is less expensive or if the final product streams have the properties as desired. The feed can be a pure composition, a mix of solids and reactant gases, a mix of solids and reactant liquids, a mix of solids, a mix of liquids
30 and gases, a mix of liquids, a mix of gases, a mix of solids, liquids and gases, or combinations thereof. In one preferred embodiment, essentially the only constituent atoms present in the feed other than inert components are the constituent atoms

present in the desired solid product. There may be very minor impurity atoms in the feed, but undesired atoms are not present to any significant extent. As an example, if the desired oxide product is nanoscale zinc oxide (ZnO), the feed would be micron scale zinc oxide. If the desired product is indium tin oxide (ITO) the feed would be indium oxide and tin oxide. If the desired product is nonstoichiometric titanium dioxide, the feed would be titanium dioxide and the process would be run to produce a non-stoichiometric product. An example of a system which would not represent this embodiment would be the reaction of titanium tetrachloride with water to produce titanium dioxide and hydrogen chloride as follows:



In this case there are constituent atoms present in the feed, namely hydrogen and chlorine, which are not present in the desired solid product.

The preferred method is premixing the feed to as homogeneous levels as possible. However, heterogeneous, series, or parallel feeds are suitable for certain applications. The feed precursors are preferably carried in a gas or a mix of gases that does not possess or can contribute an element that is not desired in the final composition. A preferred carrier stream are inert gases such as argon, helium, neon and xenon. The powder 10 is then suspended in the gas 12, preferably in a continuous operation, using fluidized beds, spouting beds, hoppers, or combinations thereof, as best suited to the nature of the precursor. The test runs performed to reduce the invention to practice were conducted with precursor feeds having particle size greater than 1 micrometer, but the process could be used with any size suitable for its continuous vaporization in a gas stream. The resulting gas-stream suspension 16 is advantageously preheated in a heat exchanger 18 and then is fed into a thermal reactor 20 where the suspended powder particles preferably completely evaporated in a thermal evaporation zone 22 by the input of thermal energy. The dimensions of the hot zone are established based on energy balance equations derived from basic principles of transport phenomena. The temperature histories of the feed material depend upon the enthalpy of the plasma discharge and the thermodynamic properties of the feed material. The times required for heating the particulate material to the

melting point, melting, heating to the vaporization point and vaporization are calculated using heat transfer equations. Additionally, the steps of heating up to the melting temperature and boiling point, and melting and vaporization can be described using appropriate heat transfer equations. These equations can be found in the U.S. Provisional patent application Express Mail number EI813191155US dated August 26, 1997, and in Transport Phenomena in Metallurgy, G.H. Geiger and D. R. Pourier, Addison-Wesley Publishing Co., Reading, MA, USA (1973) both of which are included herein by reference. The source 24 of such thermal energy can be accomplished by external heat transfer or by internal heat or both. Examples of external heat include but are not limited to induction, d.c. arc, plasma and radiation. Examples of internal heat include, but are not limited to reaction heat such as combustion and latent heats of phase transformation. Any of these may be used so long as they are sufficient to cause the rapid vaporization of the powder suspension being processed. It is desirable that the temperature in the thermal evaporation zone be in excess of 2000 degrees C. It is preferred that the temperature in the thermal evaporation zone be in excess of 3000 degrees K. It is more preferred that the temperature in the thermal evaporation zone be in excess of 4000 degrees K. It is most preferred that the T in the thermal evaporation zone be in excess of 5000 degrees K. It is necessary that the temperature in the thermal evaporation zone be above the vaporization temperature of all constituent species. Optionally, in order to prevent contamination of the vapor stream caused by partial sublimation or vaporization of the thermal reactor's interior walls, they may be pre-coated with the same material being processed. Additionally, this problem can be prevented most preferably by actively cooling the reactor walls and by using a confinement gas stream, i.e. a blanket of the inert gases along the walls of the reactor.

The vaporized gas-stream suspension next enters an extended reaction zone 26 of the thermal reactor that provides additional residence time, as needed to complete the evaporation of the feed material and to provide additional reaction time (if necessary). It is desirable that the temperature in the extended reaction zone be in excess of 2000 degrees C. It is preferred that the temperature in the extended reaction zone be in excess of 2500 degrees K. It is more preferred that the temperature in the extended reaction zone be in excess of 3000 degrees K. It is necessary that the

temperature in the extended reaction zone be above the vaporization temperature of all constituent species. In some cases, this may mandate a temperature in excess of 3000 degrees K. As the stream leaves the reactor, it passes through a zone 56 where the thermokinetic conditions favor the nucleation of solid powders from the vaporized precursor. These conditions are determined by calculating the supersaturation ratio and critical cluster size required to initiate nucleation. Rapid quenching leads to high supersaturation which gives rise to homogeneous nucleation. The unstable vapor phase system self-nucleates on atomic clusters of critical size. Below the critical size, the clusters are unstable for a given supersaturation, while above the cluster size the free energy of the cluster is negative. For an ideal vapor phase, the radius of the critical cluster size is given by the relation

$$r_n = 2 \gamma V / k T \ln(P_i / P_\infty) \quad (2)$$

where γ is the surface free energy, V is the molecular volume of the condensed phase, k is Boltzman's constant, P_i is the pressure of the vapor in the system, and P_∞ is the vapor pressure of the condensed phase. See G. S. Springer, Advances in Heat Transfer, 14, 281-341, Academic Press (1978) which is included herein by reference.

Using titanium powder as an example, based on the physical properties of the feed material and operating conditions in the reactor (size = 10μ , melting point = $1,660^\circ\text{C}$, boiling point $3,287^\circ\text{C}$, heat of vaporization of titanium = 10.985 Btu/g , hot gas temperature = $4,000^\circ\text{C}$), it is possible to calculate the residence time required for vaporization (2.32 msec for heating to melting point, 0.265 msec for melting, 5.24 msec for vaporization; total time required = 8-10 msec). Based on the velocity of the suspension injected into the reactor and the travel distance through the reactor, one can determine that a velocity of about 46 ft/sec produces a residence time of 10.7 msec, sufficient for vaporization. If the process requires a predetermined thermokinetic state of the powder being processed which can be enhanced by the presence of a particular gas, a kinetic gas feed 28 (such as argon, helium, nitrogen, oxygen, hydrogen, water vapor, methane, air, or combinations thereof) can also be mixed with the precursor vapor to reach the desired thermokinetic state. As soon as the vapor has begun nucleation, the process stream is quenched in a converging-

diverging nozzle-driven adiabatic expansion chamber 30 at rates at least exceeding 10^3 K/sec, preferably greater than 10^6 K/sec, or as high as possible. As further detailed below, a cooling medium 32 is utilized for the converging-diverging nozzle to prevent contamination of the product and damage to the expansion chamber 30.

5 Additionally, the use of a confinement blanket gas stream all along the periphery of the product stream also prevents the deposition of nanometer clusters to the walls of the reactor from thermophoresis. Rapid quenching ensures that the powder produced is homogeneous, its size is uniform and the mean powder size remains in submicron scale. The quenching of the product gas, however, can be accomplished in numerous
10 ways and combinations thereof. Some additional examples include, but are not limited to, addition of coolant gases or liquids, addition of materials which absorb heat, radiative cooling, conductive cooling, convective cooling, application of a cooled surface, impinging into liquid such as but not limited to water. The preferred method however, is gas expansion as is described in detail below.

15 The theoretical behavior of the Joule-Thompson adiabatic expansion process is described by the well-known equation:

$$T_2/T_1 = (P_2/P_1)^{(k-1)/k}, \quad (3)$$

20 where T_1 and T_2 are the temperatures before and after expansion, respectively; P_1 and P_2 are the pressures before and after expansion, respectively; and k is the ratio of specific heats at constant pressure and constant volume (C_p/C_v).

Applying Equation 2 to a temperature change occurring during adiabatic expansion,
25 ΔT ,

$$\Delta T/T_1 = (T_2 - T_1)/T_1 = (P_2/P_1)^{(k-1)/k} - 1; \quad (4)$$

or, for a steady state process,

30

$$dT/dt = T_1 d[(P_2/P_1)^{(k-1)/k}]/dt, \quad (5)$$

which suggests that Joule-Thompson expansion can quench high-temperature vapors at a steady-state quench rate that depends on the rate at which the pressure is reduced across a given adiabatic expansion device. Thus, in a continuous, steady-state process, the quench rate can be changed by changing the rate of expansion, which provides a much-sought form of control over the nucleation process of nanopowders produced by vapor condensation. Since it is known that the size, size distribution and other properties of vapor condensation products depend on the speed at which the nucleating material is quenched, the adiabatic expansion approach of the present invention provides an invaluable tool, missing in all prior-art processes, for controlling the quality of the resulting nanopowders. In addition, because the process can be carried out stably in continuous fashion, it provides a suitable vehicle for large scale applications and commercial production of bulk nanomaterials.

Figure 2a is a sketch of a converging-diverging nozzle 50 to illustrate the relationship between critical parameters of the process and of the nozzle used to carry out the invention. It consists of an optimally-shaped combination of a convergent section 52, a throat section 54, and a divergent section 56. At steady state, the condensing fluid is restricted through a uniformly decreasing cross-section A_1 from an initial cross-section A_1 at pressure P_1 and temperature T_1 , it is passed through the cross-section A^* of the throat 54, and then it is expanded through a final cross-section A_2 at pressure P_2 and temperature T_2 . The process is carried out through a cross-section A that is first uniformly decreasing and then uniformly increasing through the device. In the converging section 52, the Mach number M for the nozzle is less than 1, while it is equal to 1 in the throat 54, and greater than 1 in the diverging section 56. (Mach number is defined as the ratio of the hydrodynamic flow velocity to the local speed of sound.) Therefore, the initial subsonic flow is accelerated in the converging section of the nozzle, and the flow expands supersonically in the divergent section of the nozzle. At any cross-section A , the Mach number is given by the local value of A/A^* , with $m=1$ at the throat. Provided the flow is accelerated to a uniform design Mach number, the extent of cooling, pressure, and density drop can be predicted by the following one-dimensional relationships:

$$T_2/T_1 = [1 + (k-1)M^2/2]^{-1} \quad (6)$$

$$P_2/P_1 = [1 + (k-1)M^2/2]^{k/(k-1)} \quad (7)$$

$$\rho_2/\rho_1 = [1 + (k-1)M^2/2]^{1/(k-1)} \quad (8)$$

5 where T_2 , P_2 and ρ_2 are the flow temperature, pressure and density of the condensing fluid after the divergent section, T_1 , P_1 and ρ_1 , are at the inlet section of the nozzle, M is the Mach number, and K is the ratio of heat capacities at constant pressure and constant volume (C_p/C_v). See J.D. Anderson, Modern Compressible Flow, McGraw-Hill, N.Y., N.Y., (1990) which is included herein by reference.

10 Based on these equations, it is clear that the dimensions of the nozzle are key to its performance as a quenching device. In particular, by the selection of diameter and length of the three critical sections (52, 54 and 56) and the convergent and divergent angles of the corresponding sections, it is possible to design a nozzle that will produce the necessary Mach number to yield the desired quenching rate. A simple drawing of
15 such a converging-diverging nozzle is also shown in Fig. 2b to illustrate the key design parameters of the device. They are the diameter D_c , the length L_c and the converging angle Θ_c , for the converging section; the diameter D_d , the length L_d and the diverging angle Θ_d for the diverging section; and the diameter D_t , and length L_t , for the throat. In the preferred embodiment of the invention, the dimensions used on
20 the basis of the previously stated equations were as follows: $D_c = 3.0$ in, $L_c = 4.125$ in, $\Theta_c = 17.965^\circ$, $D_d = 0.75$ in, $L_d = 1.261$ in, $\Theta_d = 9.648^\circ$, $D_t = 0.325$ in, and $L_t = 0.114$ in.

For example, using argon as the medium, with a pressure drop of 0.72 atmospheres across the nozzle, a temperature drop of $T_2/T_1 = 0.54$ can be expected
25 across the nozzle. It should be noted that in the preferred nozzle, as further detailed below, besides the cooling effect due to expansion, the temperature drop across the nozzle is also enhanced by heat transfer with a boundary-layer gas blanket in the nozzle and by water cooling of the nozzle itself.

Referring back to Figs. 3a, 3b and 3c, the particulars of the nozzle 50 of the
30 invention, as adapted to a process for rapidly quenching condensing vapors to produce nanopowders, are illustrated in sectional-elevational and top views. For durability and continuous operation, it is necessary to keep the nozzle wall cool to

avoid contamination of the quenched product with the material of construction of the nozzle or, in worst cases, even to avoid melt down and structural failure of the nozzle. Keeping the nozzle wall cool enhances the quenching effect of the nozzle, leading to yet higher quench rates (exceeding 10^6 K/sec). Accordingly, as shown in Figure 3a, the temperature of the nozzle is maintained low with a coolant stream 32, such as cooling water, circulating in a cooling jacket 29 surrounding the nozzle's interior wall 58 between inlet and outlet ports 60 and 62. The cooling medium is preferably circulated in countercurrent flow to optimize uniform cooling of the wall.

In addition, although lower nozzle-wall temperatures improve the contamination and failure problems, such lower temperatures can also lead to vapor condensation on the nozzle walls because of mechanisms such as thermophoresis. Vapor condensation can, in turn, lead to increasing restriction in the nozzle throat diameter, with subsequent closure of the throat and failure of the nozzle. We solved this additional problem by providing a gaseous boundary-layer stream 33 to form a blanket over the internal surface of the nozzle. As shown in Figure 3c, the blanket gases can be introduced into the nozzle's interior wall axially, radially or tangentially, through an inlet port 31, and can be inert, such as argon or helium when metals and alloys are being processed; or reactive, such as nitrogen, when nitrides are being synthesized; or oxygen or air, when oxides are being processed; methane and hydrocarbons, when carbides are being processed; halogens when halides are being synthesized; or combinations thereof, depending on the ultimate material being synthesized. Thus, reactive gases can participate in heat transfer with the nucleation process, or reactively on powder surface to selectively modify the composition of the surface (coated powders), or reactively to transform the bulk composition of the powder, or in combinations to achieve multiple functions. This secondary gas feed 33 can help engineer the product nucleation process and the resultant characteristics of the powder. Such nanosize powders will be passivated by precision controlled exposure to N_2 , O_2 , CH_4 or NH_3 .

Referring back to Figure 1, the quenched gas stream 34 is then filtered in appropriate separation equipment 36 to remove the submicron powder product 38 from the gas stream. The separation can be accomplished using various methods including, but not limited to, bag houses containing polymeric or inorganic filters,

electrostatic filtration, surface deposition on cold surfaces followed by scraping with a blade, centrifugal separation, in situ deposition in porous media, adsorption in liquids or solids. The preferred method for use in the present invention, however, is the use of bag houses. As well understood in the art, the filtration can be accomplished by
5 single stage or multistage impingement filters, electrostatic filters, screen filters, fabric filters, cyclones, scrubbers, magnetic filters, or combinations thereof. The filtered nanopowder product 38 is then harvested from the filter 36 either in batch mode or continuously using screw conveyors or phase solid transport and the product stream is conveyed to powder processing or packaging unit operations (not shown in
10 the drawings). The filtered gas stream 40 is compressed in a vacuum-pump/compressor unit 42 and cooled by preheating the gas-stream suspension 16 in heat exchanger 18. Thus, the enthalpy of compression can be utilized by the process as process heat through heat integration. Stream 40 is then treated in a gas cleaning unit 44 to remove impurities and any undesirable process product gases (such as CO,
15 CO₂, H₂O, HCl, NH₃, etc). The gas treatment can be accomplished by single stage or multistage gas-gas separation unit operations such as absorption, adsorption, extraction, condensation, membrane separation, fractional diffusion, reactive separation, fractional separation, and combinations thereof. Finally, the treated gases 46 are recycled back to be reused with the feed gas stream 12. A small split stream 48
20 of the compressed treated gas 46 is purged to ensure steady state operation of the continuous thermal process.

Additionally, the invention was reduced to practice in a pilot plant illustrated schematically in Fig. 4. This thermal reactor, system consists of an upper, cylindrical, thermal evaporation chamber 22 made of quartz and cooled by circulating water (not
25 shown). The gas-stream suspension 16 is formed by mixing the solid feed material 10 fed by a powder feeder 11 with an inert gas stream 12, such as argon. The suspension 16 is injected continuously from the top of the thermal evaporation chamber 22 through a water-cooled injection probe 23 and it is heated inductively by means of a DC plasma torch. Note that for the smaller scale process an ICP torch was used as the
30 heat torch. However, one problem associated with the ICP torch is its low thermal efficiency. For scaled up processes, the use of a DC plasma torch is more advantageous because it enables better thermal efficiency, higher feed rates, no RF

radiation shielding is required, and it is easily positionable as compared to the ICP torch. In a DC plasma torch, plasma is produced by electrical discharge between two electrodes in the presence of a gas. The classifications of plasma torches are based on the position of electrodes, for example, non-transferred or transferred arc modes. In the non-transferred arc mode, both the anode and the cathode are located in the torch and the arc is established between these electrodes. In the transferred arc mode, one electrode is located outside the torch, which may be the workpiece or material to be heated. In the scaled-up nanosize metal powders production unit, a non-transferred arc DC thermal plasma torch will be used as the heat source. The reactor also comprises another, cylindrical, extended reaction zone 26 made of stainless steel, water cooled, positioned downstream of the thermal evaporation zone 22, and sufficiently large to give the feed stream the residence time required to complete the vaporization and reaction. The reaction zone 26 is lined with a zirconia refractory felt and a layer of silicon-carbide refractory material to reduce heat losses from the hot reaction zone. If necessary to prevent contamination of the reacting fluid by the reactor or refractory material, the reactor's interior walls (and refractory lining) may be further lined with the same material constituting the solid feed.

The adiabatic expansion chamber 30 consists of a converging-diverging nozzle, as illustrated in Fig. 3a, operated with a pressure drop (created by the vacuum pump 42 operated at 50 to 650 Torr) sufficient for quenching the high-temperature vapors produced by plasma induction upstream in the reactor. The theoretical behavior or the Joule Thompson adiabatic expansion process has already been described above. After rapid quenching leading to homogeneous nucleation and nanosized powders, the powders are passivated by precision controlled exposure to N_2 , O_2 , CH_4 or NH_3 . The separation system of the invention is realized by means of a collection chamber 35, attached to the outlet of the expansion chamber 30, where the very fine particles entrained in the gaseous stream are collected on a water-cooled metallic coil 37 (copper was used successfully for the test runs detailed below) and periodically extracted. It is anticipated that commercial-scale equipment would incorporate a screw or similar conveyor for the continuous removal of the nanopowder product from the collection chamber 35. The gas stream 40 out of the collection chamber is further passed through a filter 39 and trap 41 to thoroughly clean it prior to passage

through the vacuum pump 42. A monitor and fluid-control panel 43 is utilized to monitor process variables (temperatures, pressures, water and gas flow rates), record them, and control all water and gas streams to maintain steady-state operation. It is noted that for simplicity the gas stream 48 exhausted from the vacuum pump 42 was not recycled in the demonstration plant of Fig. 4, but a commercial application would preferably do so for energy and material conservation. Additionally, Figures 5a, 5b, 5c, and 5d show the preferred embodiment of the present invention for a scaled up process.

Additionally, towards one of the goals of the present invention to produce a cost effective process, a detailed engineering cost analysis of the thermal process was performed for nanosize passivated aluminum powder. The results of the analysis suggested that the future total product cost for nanosize aluminum powder will be about 47.00/lb, therefore the first estimate for future nanosize aluminum powder market price was assessed at about 82.00/lb.

The effectiveness of the invention was demonstrated by utilizing the system of Fig. 2 to produce nanosize powders of several different materials. In each case, the powders harvested were characterized for phases, size, morphology, and size distribution. X-ray diffraction (XRD) was used to determine the phases present in the samples using a Siemens D5000 diffractometer with Ni-filtered Cu K α radiation. The peak widths for average grain size analysis were determined by a least-square fit of a Cauchy function. The average size of the powder produced was estimated by Scherrer's method. Transmission electron microscopy (Hitachi TEM H-8100 equipped with a Kevex® EDX) was used for size, morphology, and size distribution. The particle size of the powders produced was in the manometer range. Scanning electron microscopy (SEM) was used for the coarser size feed powders.

Example 1

Zinc: Commercially available zinc powder (-325 mesh) was used as the precursor to produce nanosize zinc powder. Feed zinc powder was fed into the thermal reactor suspended in an argon stream (argon was used as the plasma gas; the total argon flow rate was 2.5 ft³/min). The reactor was inductively heated with 16 kW of RF plasma to

over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250-Torr, but useful results were obtained at different pressure drops, ranging from 100 to 550 Torr. After undergoing a pressure drop of 100 to 550 Torr through the converging-diverging nozzle, the powder produced was separated from the gas by means of a cooled copper-coil-based impact filter followed by a screen filter. Fig. 6 is the TEM micrograph (or nanograph) of the nanosize powder produced by the invention, showing it to be in the 5-25 nanometer range. The size distribution was narrow, with a mean size of approximately 15 nm and a standard deviation of about 7.5 nm. Variations in the operating variables (such as power input, gas pressure, gas flow rates, and nozzle throat size) affected the size of the powder produced. An XRD pattern of the product is shown in Fig. 7, which indicates that the only phase present was zinc. To avoid condensation at the wall, argon was introduced tangentially (radial or axial injections have also been proven to be effective) at the nozzle walls. The inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

Example 2

Iron-Titanium Intermetallic: 2-5 micron powders of iron and 1025 micron powders of titanium were mixed in 1:1 molar ratio and fed into the thermal reactor suspended in an argon stream (total gas flow rate, including plasma gas, was 2.75 ft³/min). The reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and above 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 550 Torr. After undergoing a pressure drop of 100 to 550 Torr through the converging-diverging nozzle, the powder produced was separated from the gas by means of a cooled copper-coil-based impact filter followed by a screen filter. Fig. 8 is the SEM micrograph of the feed powders used, showing that they were greater than 1

micrometer when fed. Fig. 9 is a TEM image of nanopowders produced by the invention, showing them to be in the 10-45 nanometer range. The size distribution was narrow, with a mean size of approximately 32 nm and a standard deviation of about 13.3 nm. Variations in the operating variables affected the size of the powder produced. The XRD pattern of the product is shown in Fig. 10, which indicates that the phases formed were titanium, iron and iron-titanium intermetallic (FeTi). The phases present illustrate that the invention can produce nanoscale powders of metals and intermetallics. To avoid condensation at the wall, argon was introduced tangentially (radial or axial injections have also been proven to be effective) at the nozzle walls. The inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

Example 3

Nickel-Aluminum Intermetallic: 1-4 micron powders of nickel and 10-30 micron powders of aluminum were mixed in 1:1 molar ratio and fed into the thermal reactor suspended in an argon stream (total feed, including plasma gas, at 2.75 ft³/min). The reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and above 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 550 Torr. The powder produced was separated from the gas by means of a cooled copper-coil-based impact filter followed by a screen filter. Fig. 11 is a TEM image of the nanopowder produced by the invention, showing it to be in the 10-30 nanometer range. The size distribution was narrow, with a mean size of approximately 16.4 nm and a standard deviation of about nm. Variations in the operating variables affected the size of the powder produced. The XRD pattern of the product is shown in Fig. 12, which indicates that the phase formed was NiAl. The phases present illustrate that the invention can produce nanoscale powders of metals and intermetallics. To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The

inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

Example 4

5

Tungsten Oxide: Commercially available tungsten oxide powder (-325 mesh size) was used as the precursor to produce nanosize WO_3 . The tungsten oxide powder was suspended in a mixture of argon and oxygen as the feed stream (flow rates were 2.25 ft^3/min for argon and 0.25 ft^3/min for oxygen). The reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 550 Torr. After undergoing a pressure drop of 100 to 550 Torr through the converging-diverging nozzle, the powder produced was separated from the gas by means of a cooled copper-coil-based impact filter followed by a screen filter. Fig. 13 is the TEM nanograph of the WO_3 powder produced by the invention, showing it to be in the 10-25 nanometer range. The size distribution was narrow, with a mean size of about 16.1 nm and a standard deviation of about 6.3 nm. Variations in the operating variables (such as power input, gas pressure, gas flow rates, and nozzle throat size) affected the size of the powder produced. An XRD pattern of the product is shown in Fig. 14, which indicates that the phase present was WO_3 . To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

10

15

20

25

Example 5

Cerium Oxide: Commercially available cerium oxide powder (5-10 micron size) was used as the precursor to produce nanosize CeO_2 . The cerium oxide powder was suspended in a mixture of argon and oxygen as the feed stream (at total rates of 2.25 ft^3/min for argon and 0.25 ft^3/min for oxygen). The reactor was inductively heated

30

with 18 kW of RF plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 650 Torr. The powder produced was separated from the gas by means of a cooled copper-coil-based impact filter followed by a screen filter. Fig. 15 is the TEM nanograph of the CeO_2 powder produced by the invention, showing it to be in the 5-25 nanometer range. The size distribution was narrow, with a mean size of about 18.6 nm and a standard deviation of about 5.8 nm. Variations in the operating variables affected the size of the powder produced. An XRD pattern of the product is shown in Fig. 16, which indicates that the phase present was CeO_2 . To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

15

Example 6

Silicon Carbide: Commercially available silicon carbide powder (-325 mesh size) was used as the precursor to produce nanosize SiC. The powder was suspended in argon as the feed stream (total argon flow rate of 2.5 ft³/min). The reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 550 Torr. The powder produced was separated from the gas by means of a cooled copper coil based impact filter followed by a screen filter. Fig. 17 is the TEM nanograph of the SiC powder produced by the invention, showing it to be in the 10-40 nanometer range. The size distribution was narrow, with a mean size of approximately 28 nm and a standard deviation of about 8.4 nm. Variations in the operating variables affected the size of the powder produced. An XRD pattern of the product is shown in Fig. 18, which indicates that the phase present was SiC. To avoid condensation at the wall, argon

30

was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

Example 7

5

Molybdenum Nitride: Commercially available molybdenum oxide (MoO_3) powder (325 mesh size) was used as the precursor to produce nanosize Mo_2N . Argon was used as the plasma gas at a feed rate of $2.5 \text{ ft}^3/\text{min}$. A mixture of ammonia and hydrogen was used as the reactant gases (NH_3 at $0.1 \text{ ft}^3/\text{min}$; H_2 at $0.1 \text{ ft}^3/\text{min}$). The reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 550 Torr. The powder produced was separated from the gas by means of a cooled copper coil based impact filter followed by a screen filter. Fig. 19 is the TEM nanograph of the Mo_2N powder produced by the invention, showing it to be in the 5-30 nanometer range. The size distribution was narrow, with a mean size of about 14 nm and a standard deviation of about 4.6 nm. Variations in the operating variables affected the size of the powder produced. An XRD pattern of the product is shown in Fig. 20, which indicates that the phase present was Mo_2N . To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

25

Example 8

Nickel Boride Ceramic: 10 50 micron powder of nickel boride were fed into the thermal reactor with argon (fed at a total rate, including plasma gas, of $2.75 \text{ ft}^3/\text{min}$). once again, the reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging diverging nozzle. The preferred pressure drop across the nozzle was

250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 550 Torr. The powder produced was separated from the gas by means of a cooled copper coil based impact filter followed by a screen filter. Fig. 21 shows the SEM micrograph of the feed powders used, demonstrating that they were greater than 1 micrometer when fed. Fig 22 is the TEM nanograph of the Ni_3B powder produced by the invention, showing it to be in the 10 to 30 nanometer range. The size distribution was narrow, with a mean size of about 12.8 nm and a standard deviation of about 4.2 nm. Variations in the operating variables affected the size of the powder produced. An XRD pattern of the product is shown in Fig. 23, which indicates that the phase present were Ni and Ni_3B . To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

Example 9

Oxide Ceramics: 5-10 micron powders of calcium carbonate were fed into the thermal reactor with argon (at 2.5 ft^3/min). The reactor was inductively heated with 16 kW of RF plasma to over 5,000 K in the plasma zone and about 2,500 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched by thermal expansion to about 100 Torr. The pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 50 to 550 Torr. The powder produced was separated from the gas by means of a cooled copper coil based impact filter followed by a screen filter. Fig. 24 is the TEM image of powder produced by the invention, showing it to be in the 5 to 20 nanometer range. As expected from the calcination reaction occurring in the reactor, the XRD data (shown in Fig. 25) established that the main phase of the nanopowder was CaO. Some other phases, such as $\text{Ca}(\text{OH})_2$, were also present due to exposure to atmospheric moisture. The size distribution of the CaO was narrow, with a mean size of about 14.8 nm and standard deviation of about 3.8 nm.

An alternate run was made with MgCO_3 powders with mean size of about 7 microns processed with argon. Once again, nanoscale powders of MgO were

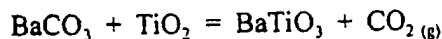
produced as evidenced by TEM and XRD data. The final product powder size was observed to vary with changes in the pressure, temperature, flow rate, and compositions.

Example 10

Barium titanate (BaTiO_3): Commercially available barium titanate, micron size (5-10 micron) was used as the precursor to produce nanosize barium titanate powder. The feeding was calibrated to this required feed rate by adjusting the power feeder and the flow rate of the carrier gas. The reactor was inductively heated with 18 kW of RF plasma to a thermal steady state. Thermal steady state was established by monitoring the temperature in the reactor. Feed barium titanate powder was feed into the thermal reactor suspended in an argon stream at a gas flow rate of 1.0 ft.³/min. The power was turned off and the system allowed to cool down under inert conditions by keeping some flow of argon in the reactor. The product was collected from the quench section and filter, weighed and saved for analysis and performance testing. TEM images of the powder produced are shown in Figures 26a and 26b. The X-ray diffraction pattern of the powder produced is shown in Figure 27.

An alternate run was made with strontium titanate (SrTiO_3) powder to produce nanosize SrTiO_3 powder. The feed precursor for strontium titanate was micron size (5-10 microns) SrTiO_3 powder. TEM images of the produced powder are shown in Figures 28a and 28b. X-ray diffraction pattern of the powder produced is shown in Figure 29, which reveals that the main phase present is SrTiO_3 . The surface area of the powder produced was 22.3 m²/g. Most of the produced powder ranged from 10-40 nm.

Additionally, another run was performed to produce nanosize barium titanate (BaTiO_3) powder by the following reaction



using commercially available barium carbonate (BaCO_3) and titanium oxide (TiO_2) powders. Both precursors had a size of -325 mesh and were obtained from a commercial supplier. As a result of this test using the abovementioned thermal reactor, nanosize powder of barium titanate was produced. TEM images of the powder produced are shown in Figures 30a and 30b. Figure 31 shows the X-ray diffraction pattern of the powder produced, which shows that the main phase present is BaTiO_3 . The surface area of the produced powder was $11.9 \text{ m}^2/\text{g}$. The powder produced was in the nanosize range (10-75 nm).

10

Example 11

Nickel Zinc Ferrite: Commercially available nickel zinc ferrite powder (-325 mesh) was used as a precursor to produce nanosize $\text{NiZnFe}_2\text{O}_4$ powder. Feed $\text{NiZnFe}_2\text{O}_4$ powder was fed into the thermal reactor suspended in an argon stream (argon and helium were used as the plasma gases; the total argon flow rate was $1.6 \text{ ft}^3/\text{min}$ and the helium flow rate was $0.57 \text{ ft}^3/\text{min}$). The reactor was heated with a 25 kW DC plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 650 Torr. The powder produced was separated from the gas by means of a cooled copper coil-based impact filter followed by a screen filter. Figure 32 is the TEM nanograph of the $\text{NiZnFe}_2\text{O}_4$ powder produced by the invention, showing it to be in the 5-50 nanometer range. Variations in the operating variables affected the size of the powder produced. An XRD pattern of the product is shown in Figure 33, which indicates that the main phase present was $\text{NiZnFe}_2\text{O}_4$. To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer for any condensation on the nozzle walls.

30

Example 12

Nickel-Chromium-Cobalt-Molybdenum Alloy: Commercially available nickel-chromium-cobalt-molybdenum alloy powder (-325 mesh) was used as a precursor to

produce nanosize Ni-Cr-Co-Mo powder. Feed Ni-Cr-Co-Mo powder was fed into the thermal reactor suspended in an argon stream (argon was used as the plasma gas; the total argon flow rate was 2.5 ft³/min). The reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 650 Torr. The powder produced was separated from the gas by means of a cooled copper-coil-based impact filter followed by a screen filter. Figure 34 is the TEM nanograph of the Ni-Cr-Co-Mo powder produced by the invention, showing it to be in the 5-100 nanometer range. Variations in the operating variables affected the size of the powder produced. An XRD pattern of the product is shown in Figure 35, which indicates that the main phase present was Ni-Cr-Co-Mo with minor amounts of NiCr₂O₄ and Ni₃TiO₅. To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer for any condensation on the nozzle walls.

Example 13

Bismuth Telluride: Commercially available bismuth telluride powder (-325 mesh) was used as a precursor to produce nanosize Bi₂Te₃ powder. Feed Bi₂Te₃ powder was fed into the thermal reactor suspended in an argon stream (argon was used as the plasma gas; the total argon flow rate was 2.5 ft³/min). The reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 650 Torr. The powder produced was separated from the gas by means of a cooled copper-coil-based impact filter followed by a screen filter. Figure 36 is the TEM nanograph of the Bi₂Te₃ powder produced by the invention, showing it to be in the 20-100 nanometer range. Variations in the operating variables affected the size of the powder produced. An

XRD pattern of the product is shown in Figure 37, which indicates that the phase present was Bi_2Te_3 . To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer for any condensation on the nozzle walls.

5

These examples demonstrate the feasibility and effectiveness of the principles of this invention in producing nanosize powders from micron sized precursors. The process and apparatus of the invention, utilizing ultra rapid quenching as the process step for the formation of nanopowders, provide a practical method for controlling the size of the product by manipulating process parameters. In particular, by controlling the quenching rate by changing the pressure drop over the expansion nozzle of the invention, we found that predetermined particle sizes and size distributions can be produced reliably in a continuous, steady state process, which is easily scaleable for commercial bulk production. The process was proven viable for metals, alloys, intermetallics, ceramics, composites, and combinations thereof. In addition, we demonstrated that the process can utilize feeds of reactive components and produce submicron powders of corresponding thermodynamically stable or metastable product species at high temperatures; that it is suitable for recycling and reusing product gases as feed gases; and for recycling and reusing any unseparated product powders as feed material. The method and apparatus of the invention solve many problems unresolved by existing processes to produce submicron powders in general and nanostructured materials in particular. Especially, the process is scaleable; it is solvent free and therefore inherently non polluting and of low cost; it is flexible in relation to processing different feed materials; it allows simple control of product powder size and size distribution; and it does not utilize contaminating components in the feed or for processing, therefore yielding product powders that are as pure as the powders fed to the process.

Inasmuch as one of the primary inventive concepts of the invention is the effective thermal quenching and the attendant advantages produced by ultra rapid expansion of a vaporized suspension of the feed material, it is clear that the concept could be applied as well to a system where the precursor material is in the form of a mass evaporated by any method in a low pressure gas. Similarly, the process is

applicable to liquid or gaseous precursors that are combined with one or more reactive gases in a reactor and then quenched ultra rapidly according to the invention to produce nanosize particles with a narrow size distribution. For example, silicon tetrachloride (normally liquid at room temperature) can be reacted with methane to
5 produce a silicon carbide vapor which, rapidly quenched according to the invention, can produce a nanosize SiC powder. Similarly, silane (SiH_4 , normally gaseous at room temperature) can be reacted with methane to produce a silicon carbide vapor which can also be rapidly quenched to produce a nanosize SiC powder with a narrow size distribution. Finally, it is understood that specific changes in materials and
10 procedures may be made by one skilled in the art to produce equivalent results.

Therefore, while the present invention has been shown and described herein in what is believed to be the most practical and preferred embodiments, it is recognized that departures can be made therefrom within the scope of the invention, which is therefore not to be limited to the details disclosed herein but is to be accorded the full
15 scope of the claims so as to embrace any and all equivalent apparatus and methods.

1 What we claim is:

2

3 1. A process for producing a nanoscale powder from a precursor material
4 comprising the following steps:

5 evaporating the precursor material in a gaseous atmosphere in a thermal reactor,
6 thereby creating a vapor/gas mixture; and

7 quenching said vapor/gas mixture by effecting its expansion through a
8 predetermined pressure drop, thereby causing the formation of nanoscale particles of
9 product material in a product gas.

10

11 2. The process of claim 1, wherein said pressure drop in the quenching step is
12 sufficient to cause a temperature of the vapor/gas mixture to change at a rate of at
13 least 1,000 °C per second.

14

15 3. The process of claim 1, wherein said pressure drop in the quenching step is
16 sufficient to cause a temperature of the vapor/gas mixture to change at a rate of at
17 least 1,000,000 °C per second.

18

19 4. The process of claim 1, wherein the temperature of said thermal reactor is in
20 excess of 2000 degrees C.

21

22 5. The process of claim 1, wherein the temperature of said thermal reactor is in
23 excess of 5000 degrees K.

24

25 6. The process of claim 1, wherein the constituent atoms of said precursor material
26 consist essentially of the constituent atoms of said product material.

27

28 7. The process of claim 1, wherein said expansion through a predetermined
29 pressure drop is carried out by passing the vapor/gas mixture through a converging
30 diverging expansion nozzle.

31

- 1 8. The process of claim 7, wherein the temperature of said thermal reactor is in
2 excess of 2000 degrees C.
3
- 4 9. The process of claim 7, wherein the temperature of said thermal reactor is in
5 excess of 5000 degrees K.
6
- 7 10. The process of claim 7, wherein the constituent atoms of said precursor material
8 consist essentially of the constituent atoms of said product material.
9
- 10 11. The process of claim 7, wherein said pressure drop through the converging
11 diverging expansion nozzle is sufficient to cause a temperature of the vapor/gas
12 mixture to change at a rate of at least 1,000 °C per second.
13
- 14 12. The process of claim 7, wherein said pressure drop through the converging
15 diverging expansion nozzle is sufficient to cause a temperature of the vapor/gas
16 mixture to change at a rate of at least 1,000,000 °C per second.
17
- 18 13. The process of claim 7, wherein said pressure drop is between 50 and 650 Torr.
19
- 20 14. The process of claim 1, wherein said evaporation and quenching steps are
21 carried out on a continuous basis.
22
- 23 15. The process of claim 14, wherein said evaporation step is carried out by feeding
24 said precursor material to the thermal reactor as a suspension in said gaseous
25 atmosphere and by subjecting the suspension to an input of thermal energy.
26
- 27 16. The process of claim 15, wherein said thermal energy is at least partially
28 produced by an inductive source.
29
- 30 17. The process of claim 15, wherein said thermal energy is at least partially
31 produced by a microwave source.
32

- 1 18. The process of claim 15, wherein said thermal energy is at least partially
2 produced by an electric arc.
3
- 4 19. The process of claim 15, wherein said thermal energy is at least partially
5 produced by heat of reaction.
6
- 7 20. The process of claim 7, further comprising the step of providing a gaseous
8 boundary layer stream to form a blanket over an internal surface of the nozzle.
9
- 10 21. The process of claim 1, further comprising the step of coating an internal
11 surface of said thermal reactor with a layer of said precursor material.
12
- 13 22. The process of claim 21, wherein said expansion through a predetermined
14 pressure drop is carried out by passing the vapor/gas mixture through a converging
15 diverging expansion nozzle.
16
- 17 23. The process of claim 22, wherein said pressure drop through the converging
18 diverging expansion nozzle is sufficient to cause a temperature of the vapor/gas
19 mixture to change at a rate of at least 1,000 °C per second.
20
- 21 24. The process of claim 21, further comprising the step of providing a gaseous
22 boundary layer stream to form a blanket over an internal surface of the nozzle.
23
- 24 25. The process of claim 1, further comprising the step of separating said
25 nanoscale particles of product material from said product gas.
26
- 27 26. The process of claim 25, further comprising the step of recycling said product
28 gas by feeding the product gas to the thermal reactor with said precursor material.
29
- 30 27. The process of claim 7, wherein said nanoscale powder is free of any
31 byproducts.
32

1 28. The process of claim 7, wherein said process is a physical process.

2

3 29. A nanoscale powder having a mean size less than 100 nm and a size
4 distribution with a standard deviation less than 25 nm produced by the process of
5 claim 1.

6

7 30. A nanoscale powder having a mean size less than 100 nm and a size
8 distribution with a standard deviation less than 25 nm produced by the process of
9 claim 13.

10

11 31. A nanoscale powder having a mean size less than 100 nm and a size
12 distribution with a standard deviation less than 25 nm produced by the process of
13 claim 14.

14

15 32. A nanoscale powder having a mean size less than 100 nm and a size
16 distribution with a standard deviation less than 25 nm produced by the process of
17 claim 20.

18

19 33. A nanoscale powder having a mean size less than 100 nm and a size
20 distribution with a standard deviation less than 25 nm produced by the process of
21 claim 21.

22

23 34. A nanoscale metal alloy powder having a mean size less than 100 nm and a
24 size distribution with a standard deviation less than 25 nm produced by the process of
25 claim 1.

26

27 35. A nanoscale metal oxide powder having a mean size less than 100 nm and a
28 size distribution with a standard deviation less than 25 nm produced by the process of
29 claim 1.

30

- 1 36. A nanoscale carbide powder having a mean size less than 100 nm and a size
2 distribution with a standard deviation less than 25 nm produced by the process of
3 claim 1.
4
- 5 37. A nanoscale nitride powder having a mean size less than 100 nm and a size
6 distribution with a standard deviation less than 25 nm produced by the process of
7 claim 1.
8
- 9 38. A nanoscale ceramic powder having a mean size less than 100 nm and a size
10 distribution with a standard deviation less than 25 nm produced by the process of
11 claim 1.
12
- 13 39. A complex nanoscale powder having a mean size less than 100 nm and a size
14 distribution with a standard deviation less than 25 nm produced by the process of
15 claim 1.
16
- 17 40. A complex nanoscale powder having a mean size less than 100 nm and a size
18 distribution with a standard deviation less than 25 nm produced by the process of
19 claim 7.
20
- 21 41. A complex nanoscale powder having a mean size less than 100 nm and a size
22 distribution with a standard deviation less than 25 nm produced by the process of
23 claim 13.
24
- 25 42. A complex nanoscale powder having a mean size less than 100 nm and a size
26 distribution with a standard deviation less than 25 nm produced by the process of
27 claim 14.
28
- 29 43. A complex nanoscale powder having a mean size less than 100 nm and a size
30 distribution with a standard deviation less than 25 nm produced by the process of
31 claim 20.
32

1 44. A complex nanoscale powder having a mean size less than 100 nm and a size
2 distribution with a standard deviation less than 25 nm produced by the process of
3 claim 21.
4

5 45. Apparatus for producing a nanoscale powder from a precursor material
6 comprising, in combination: means for evaporating said precursor material in a
7 gaseous atmosphere at a predetermined minimum evaporation temperature, thereby
8 creating a vapor/gas mixture; and means for quenching said vapor/gas mixture by
9 effecting its expansion through a predetermined pressure drop, thereby causing the
10 formation of nanoscale particles of a product material.
11

12 46. The apparatus of claim 45, wherein the minimum evaporation temperature is
13 greater than 2000 degrees C.
14

15 47. The apparatus of claim 45, further comprising means for providing a gaseous
16 boundary layer stream to form a blanket over an internal surface of said means for
17 quenching the vapor/gas mixture by allowing its expansion through a predetermined
18 pressure drop.
19

20 48. The apparatus of claim 47, further comprising means for coating with a layer
21 of said precursor material an internal surface of said means for evaporating the
22 precursor material in a gaseous atmosphere.
23

24 49. A device for quenching a vapor stream of a precursor material to produce its
25 condensation into a nanoscale powder, comprising:
26 convergent means for channeling said vapor stream into a flow restriction of a
27 predetermined cross-section from an inlet zone of predetermined inlet pressure;
28 divergent means for channeling said vapor stream out of said flow restriction
29 to an outlet zone of predetermined outlet pressure; and
30 means for maintaining said inlet and outlet pressures, thereby creating a
31 pressure differential therebetween;

1 wherein said pressure differential and said cross-section of the flow restriction
2 are selected to produce a quenching of said vapor stream at a rate of at least 1.000 K
3 per second.

4

5 50. The device of claim 49, further comprising means for cooling an internal
6 surface thereof.

7

8 51. The device of claim 49, further comprising means for providing a gaseous
9 boundary-layer stream to form a gas blanket over an internal surface of the device.

10

11 52. The device of claim 49, further comprising means for cooling an internal
12 surface thereof, and means for providing a gaseous boundary-layer stream to form a
13 gas blanket over an internal surface of the device.

14

15 53. The device of claim 49, wherein said convergent means, flow restriction and
16 divergent means consist of a convergent-divergent nozzle having uniformly
17 converging and diverging sections.

18

19 54. The device of claim 53, further comprising means for cooling an internal
20 surface of the device.

21

22 55. The device of claim 53, further comprising means for introducing a reactive
23 gas into the device.

24

25 56. The device of claim 53, further comprising means for providing a gaseous
26 boundary-layer stream to form a gas blanket over an internal surface of the device.

27

28 57. The device of claim 53, further comprising means for cooling an internal
29 surface of the device, and means for providing a gaseous boundary-layer stream to
30 form a gas blanket over an internal surface of the device.

31

1 58. The apparatus of claim 45, in which said product material consists essentially
2 of nanoscale particles of said precursor material.

3
4 59. The apparatus of claim 58, wherein the minimum evaporation temperature is
5 greater than 2000 degrees C.

6
7 60. The apparatus of claim 58, further comprising means for cooling an internal
8 surface of said quenching means.

9
10 61. The apparatus of claim 58, further comprising means for providing a gaseous
11 boundary-layer stream to form a gas blanket over an internal surface of said
12 quenching means.

13
14 62. The apparatus of claim 58, further comprising means for cooling an internal
15 surface of said quenching means, and means for providing a gaseous boundary-layer
16 stream to form a gas blanket over an internal surface of said quenching means.

17
18 63. The apparatus of claim 58, further comprising means for coating with a layer
19 of said precursor material an internal surface of said means for evaporating the
20 precursor material in a gaseous atmosphere.

21
22 64. The apparatus of claim 58, further comprising means for cooling an internal
23 surface of said quenching means; means for providing a gaseous boundary-layer
24 stream to form a gas blanket over an internal surface of said quenching means; and
25 means for coating with a layer of said precursor material an internal surface of said
26 means for evaporating the precursor material in a gaseous atmosphere.

27
28 65. The apparatus claim 58, wherein said quenching means consists of a
29 convergent-divergent nozzle having uniformly converging and diverging sections.

30
31 66. The apparatus of claim 64, further comprising means for cooling an internal
32 surface of said convergent-divergent nozzle.

1 67. The apparatus of claim 64, further comprising means for providing a gaseous
2 boundary-layer stream to form a gas blanket over an internal surface of said
3 quenching means.
4

5 68. The apparatus of claim 64, further comprising means for cooling an internal
6 surface of said convergent-divergent nozzle, and means for providing a gaseous
7 boundary-layer stream to form a gas blanket over an internal surface of said nozzle.
8

9 69. The apparatus of claim 64, further comprising means for coating with a layer
10 of said precursor material an internal surface of said means for evaporating the
11 precursor material in a gaseous atmosphere at a predetermined reactor pressure.
12

13 70. The apparatus of claim 64, further comprising means for cooling an internal
14 surface of said convergent-divergent nozzle; means for providing a gaseous
15 boundary-layer stream to form a gas blanket over an internal surface of said nozzle;
16 and means for coating with a layer of said precursor material an internal surface of
17 said means for evaporating the precursor material in a gaseous atmosphere.
18

19 71. A method of quenching a high-temperature vapor of a precursor material to
20 produce a nanoscale powder thereof, comprising the following steps:

21 (a) producing a vapor stream of said high-temperature vapor from an inlet
22 zone of predetermined inlet pressure and passing said vapor stream through a
23 convergent means to channel the vapor stream into a flow restriction of a
24 predetermined cross-section;

25 (b) channeling the vapor stream out of said flow restriction through
26 divergent means to an outlet zone of predetermined outlet pressure smaller than said
27 inlet pressure; and

28 (c) maintaining said inlet and outlet pressures, thereby creating a pressure
29 differential therebetween;

30 wherein said pressure differential and said cross-section of the flow restriction are
31 adapted to produce a supersonic flow of said vapor stream.
32

1 72. The method of claim 71, wherein said pressure drop in the quenching step is
2 sufficient to cause a temperature of the vapor/gas mixture to change at a rate of at
3 least 1,000 °C per second.

4

5 73. The method of claim 71, further comprising the step of providing a gaseous
6 boundary-layer stream to form a blanket over an internal surface of the convergent
7 means.

8

9

1/34

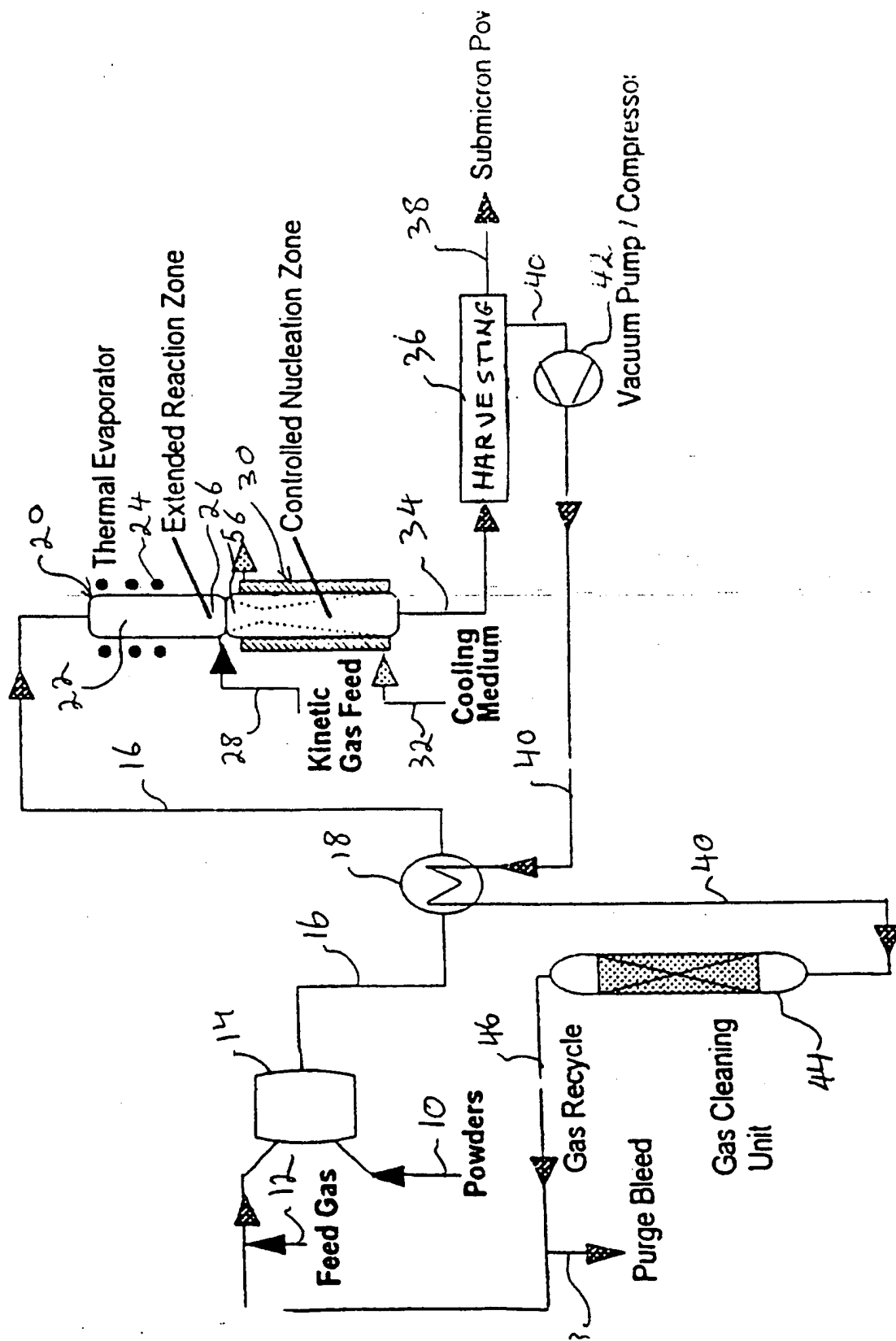


Figure 1.

2/34

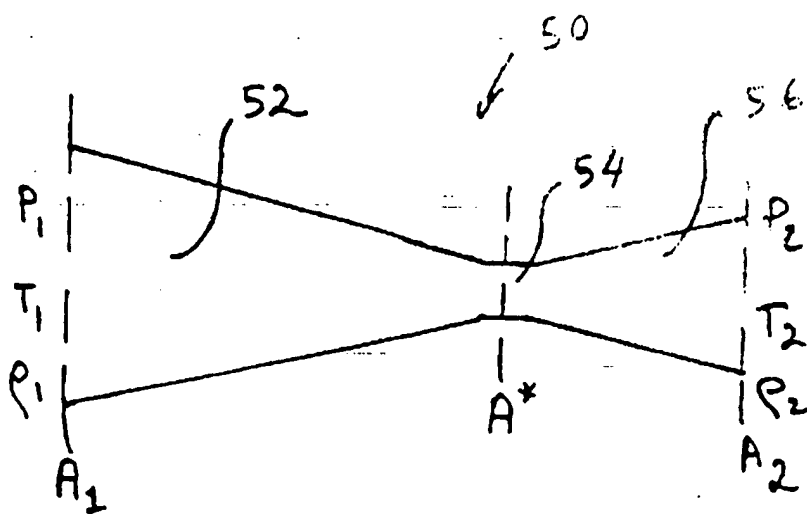
A₀

Figure 2a

3/34

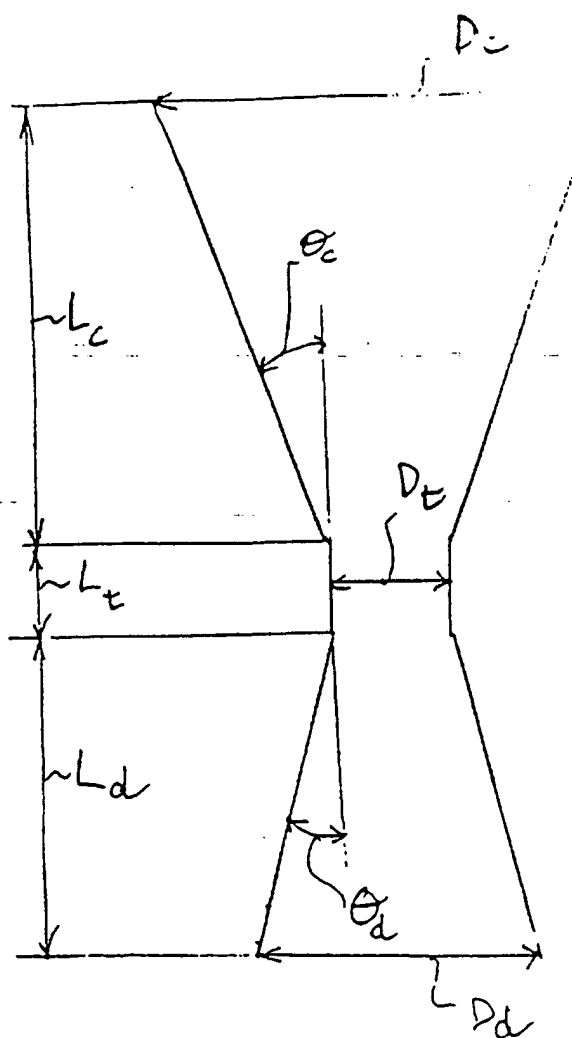


Figure 2b

4/34

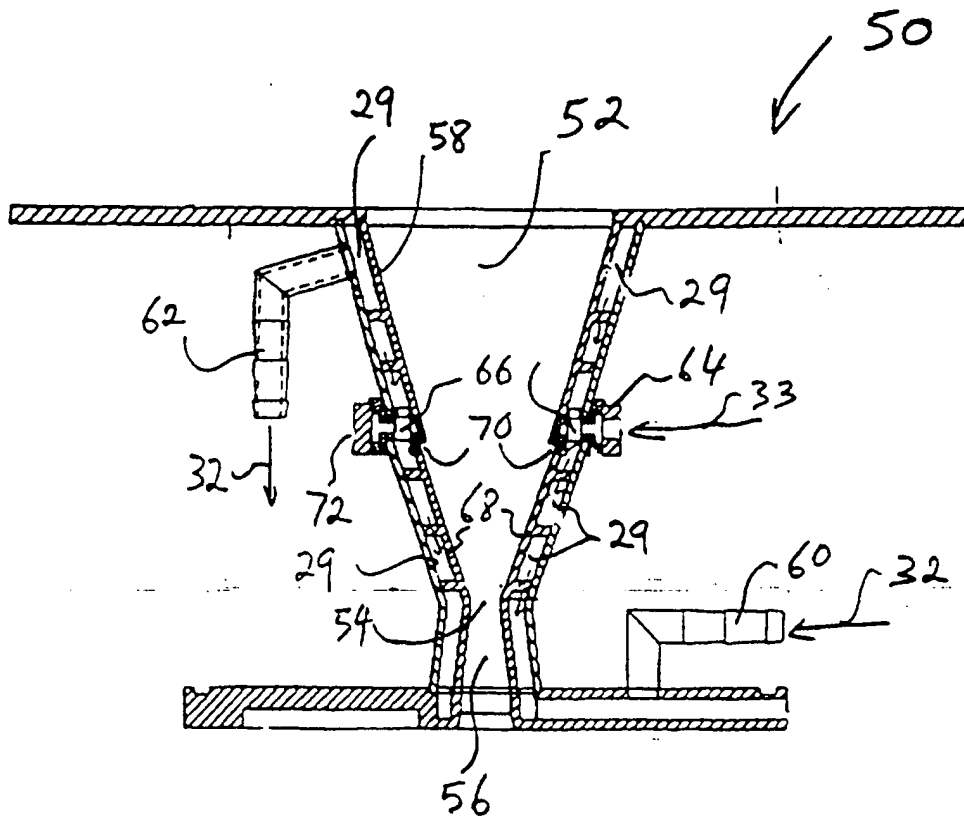


Figure 3a

5/34

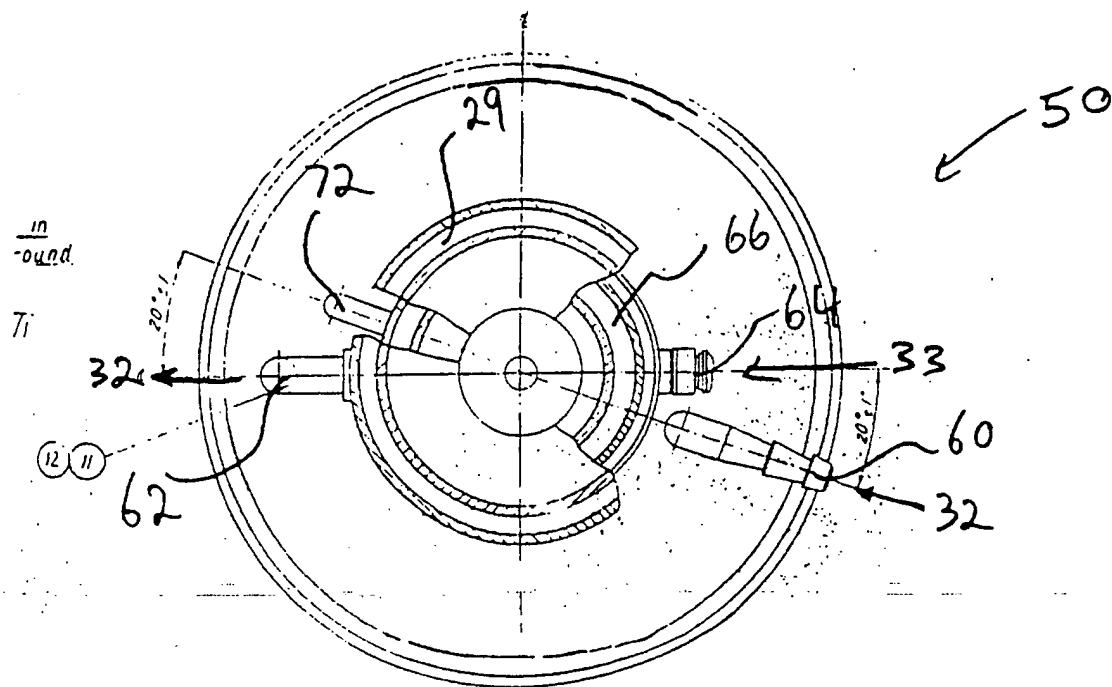


Figure 3b

6/34

50

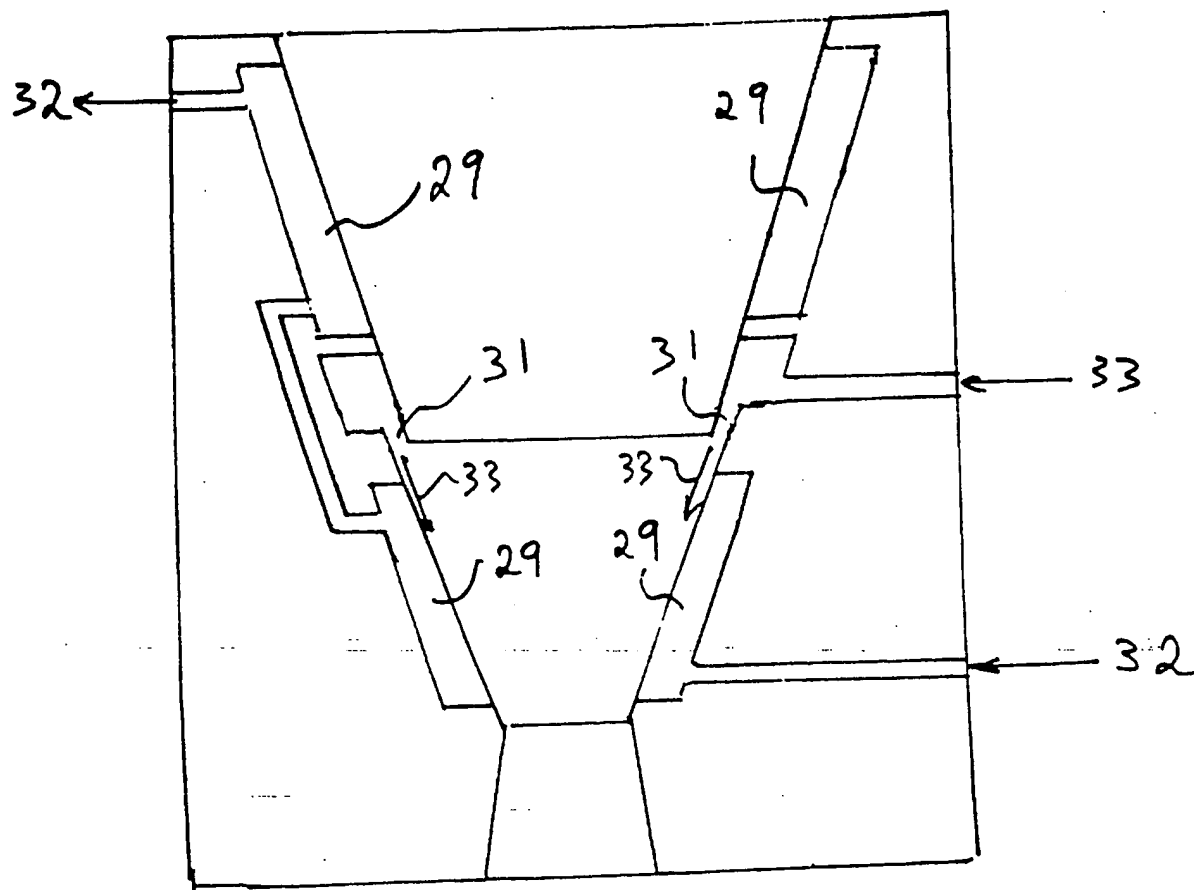


Figure 3c

7/34

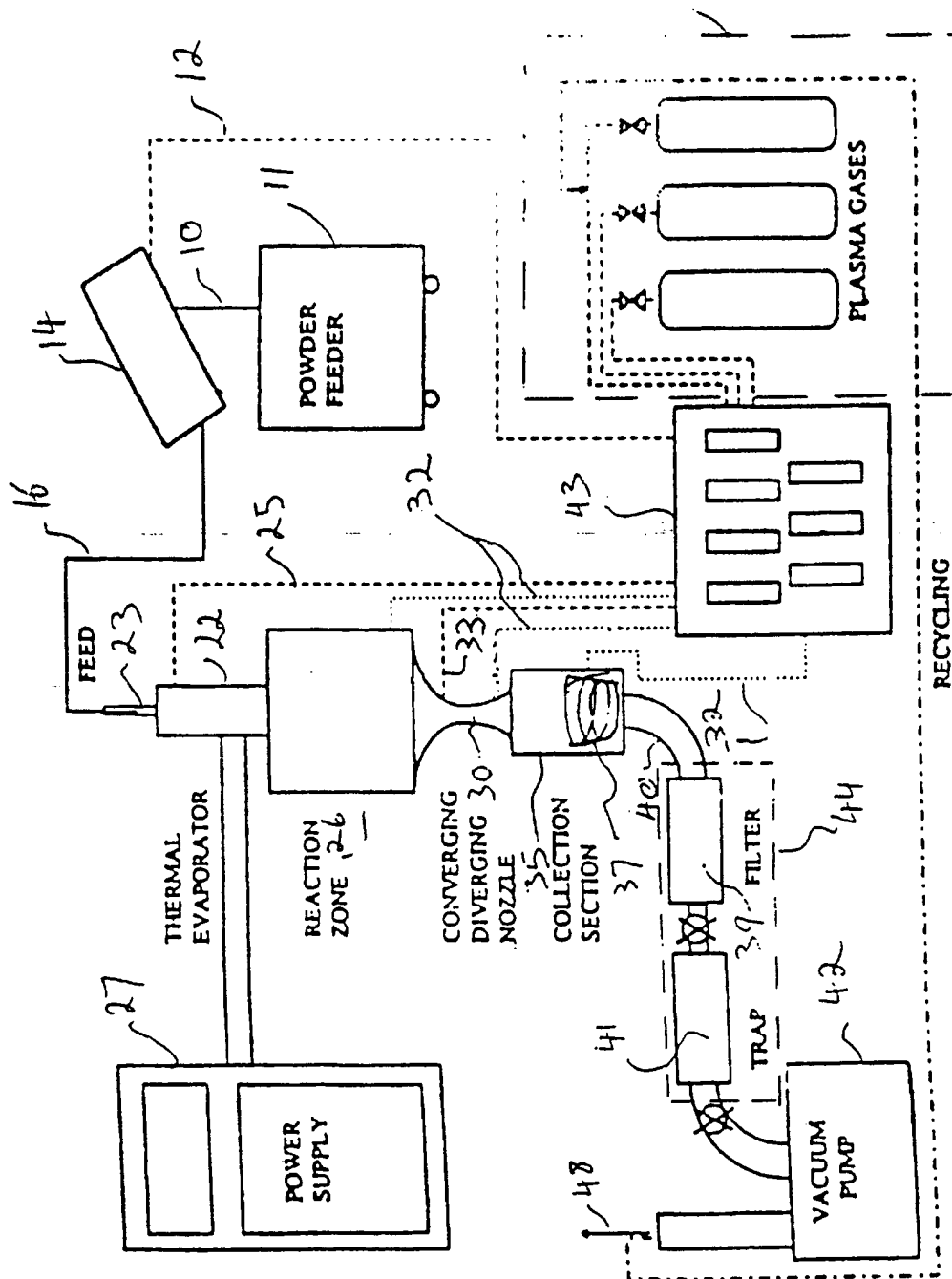


Figure 4

8/34

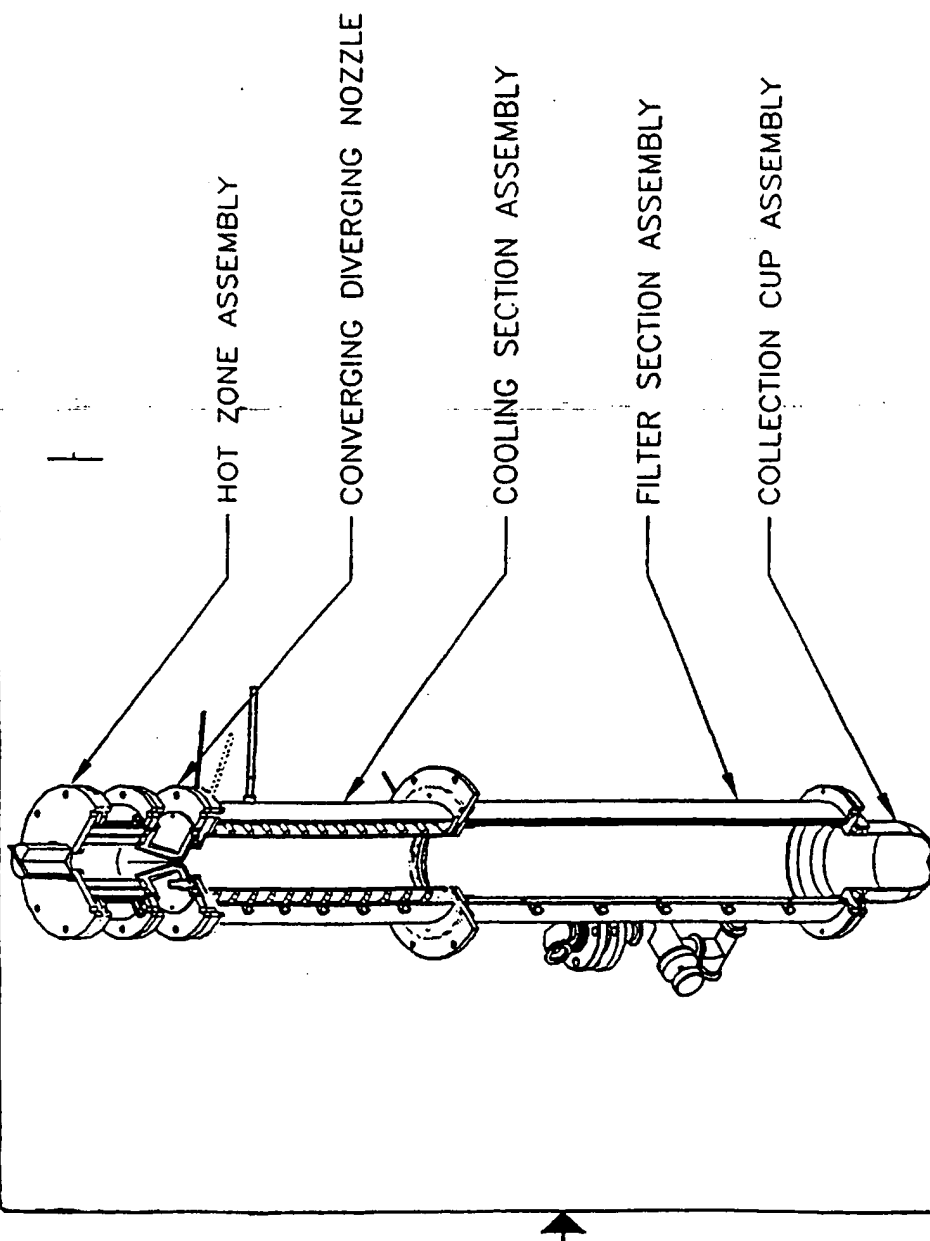
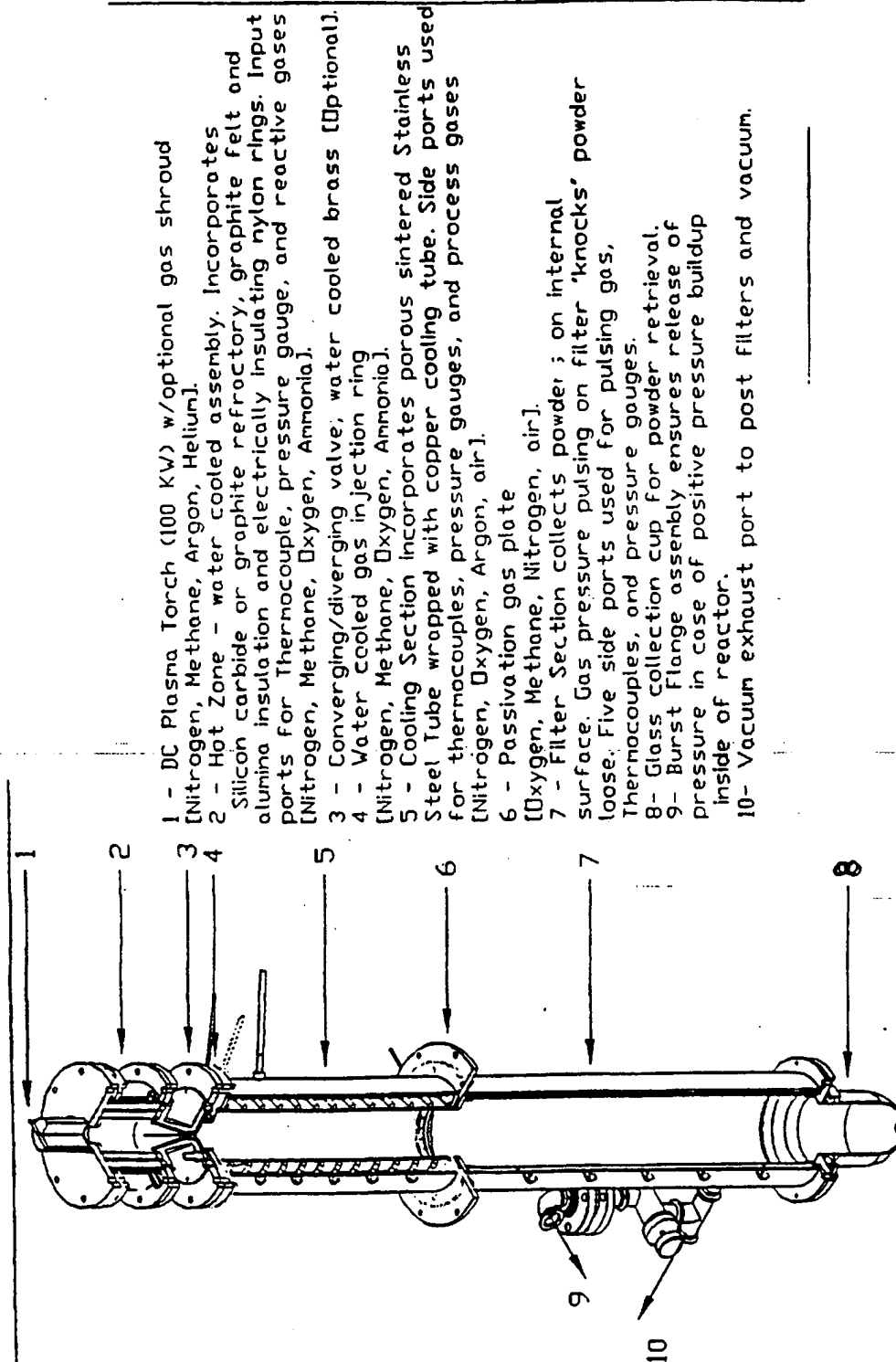


Figure 5a: DC Plasma Reactor Assembly

9/34



- 1 - DC Plasma Torch (100 KW) w/optional gas shroud [Nitrogen, Methane, Argon, Helium].
- 2 - Hot Zone - water cooled assembly. Incorporates Silicon Carbide or graphite refractory, graphite felt and alumina insulation and electrically insulating nylon rings. Input ports for Thermocouple, pressure gauge, and reactive gases [Nitrogen, Methane, Oxygen, Ammonia].
- 3 - Converging/diverging valve; water cooled brass [Optional].
- 4 - Water cooled gas injection ring [Nitrogen, Methane, Oxygen, Ammonia].
- 5 - Cooling Section incorporates porous sintered Stainless Steel Tube wrapped with copper cooling tube. Side ports used for thermocouples, pressure gauges, and process gases [Nitrogen, Oxygen, Argon, air].
- 6 - Passivation gas plate [Oxygen, Methane, Nitrogen, air].
- 7 - Filter Section collects powder; on internal surface. Gas pressure pulsing on filter 'knocks' powder loose. Five side ports used for pulsing gas, Thermocouples, and pressure gauges.
- 8 - Glass collection cup for powder retrieval.
- 9 - Burst Flange assembly ensures release of pressure in case of positive pressure buildup inside of reactor.
- 10 - Vacuum exhaust port to post filters and vacuum.

Figure 5b
DC Plasma Reactor Assembly

10/34

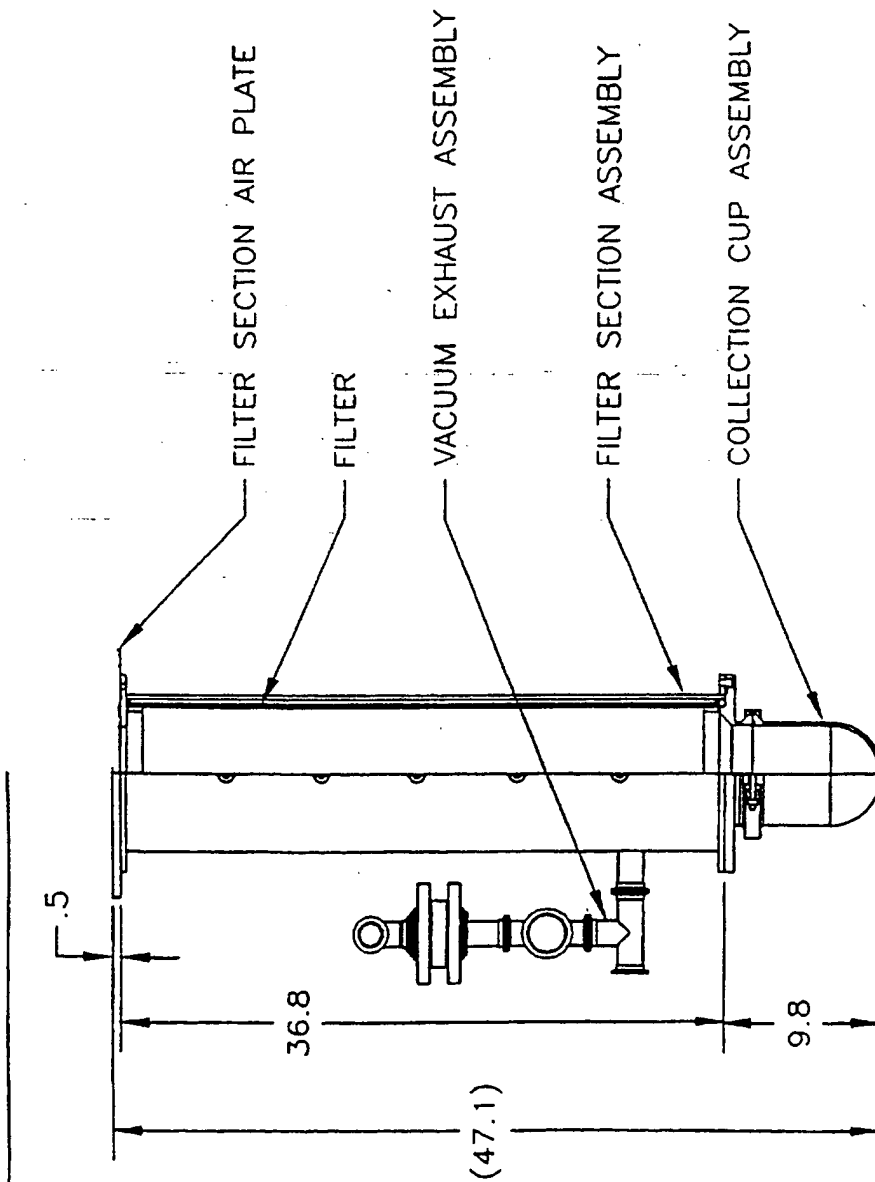
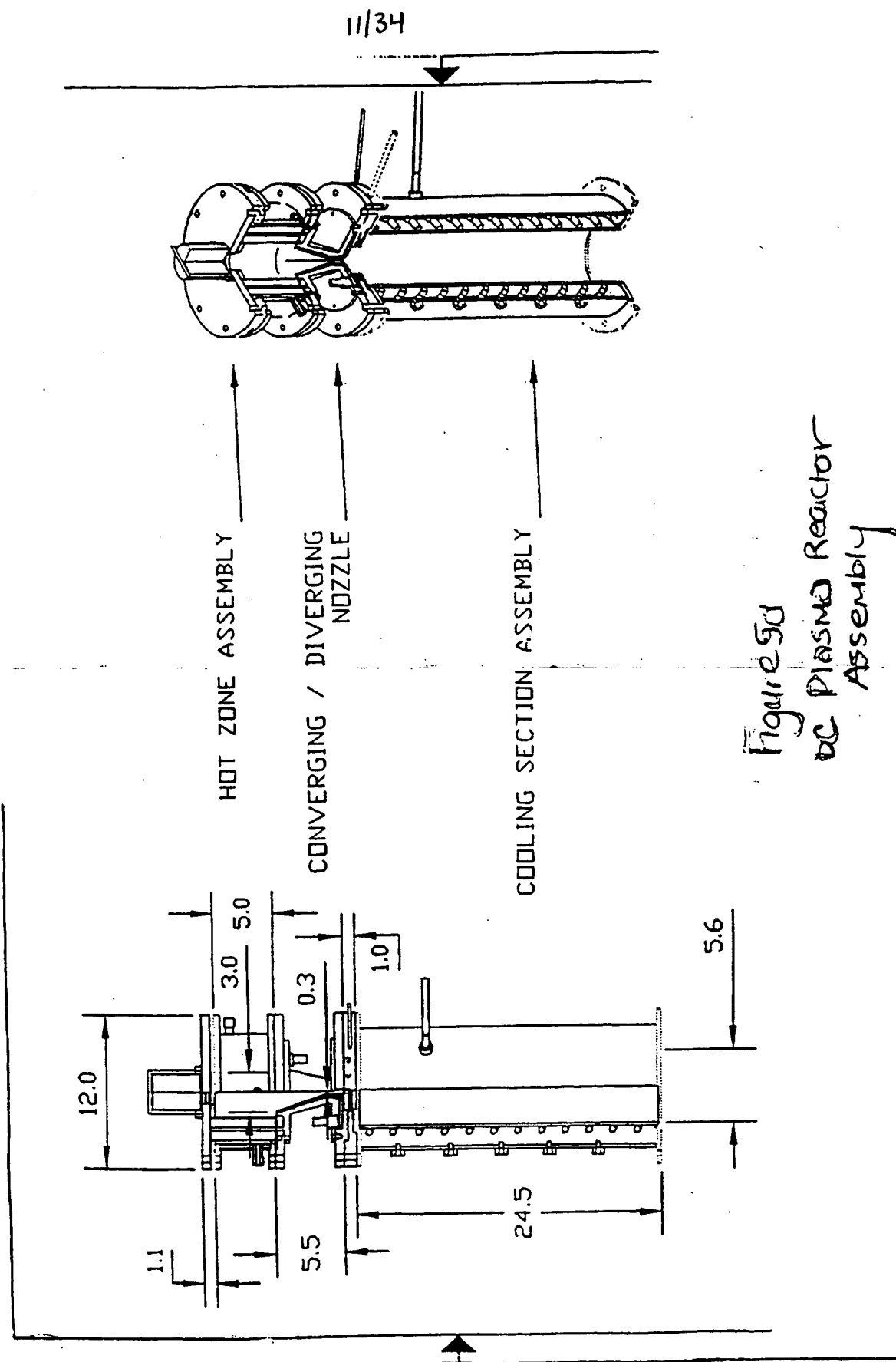


Figure 5c
DC Plasma Reactor Assembly



12/34

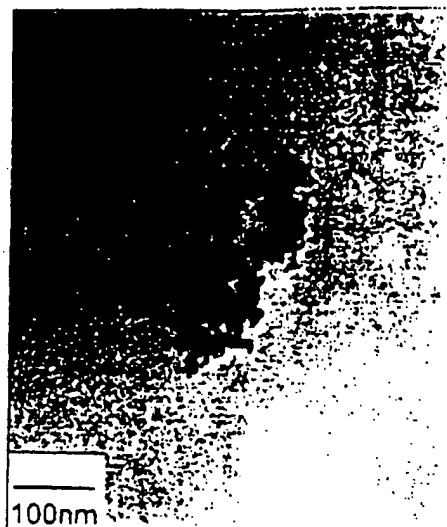


Figure 6

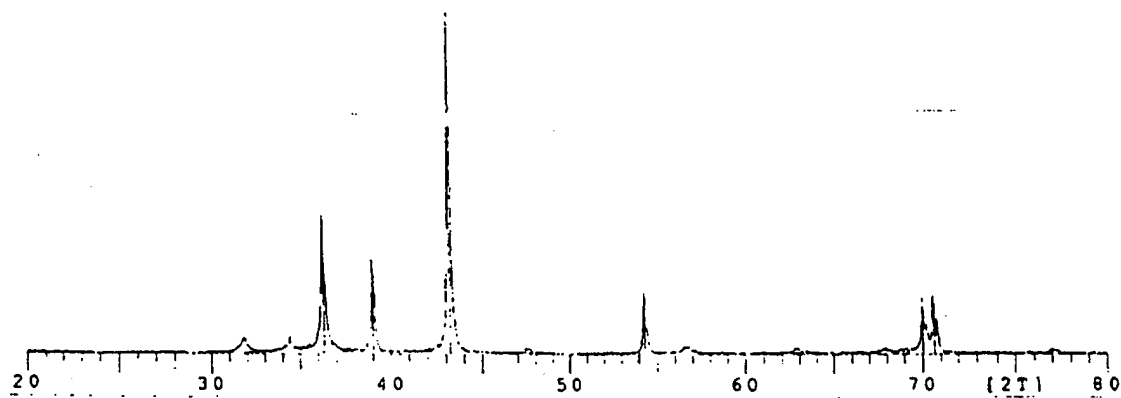
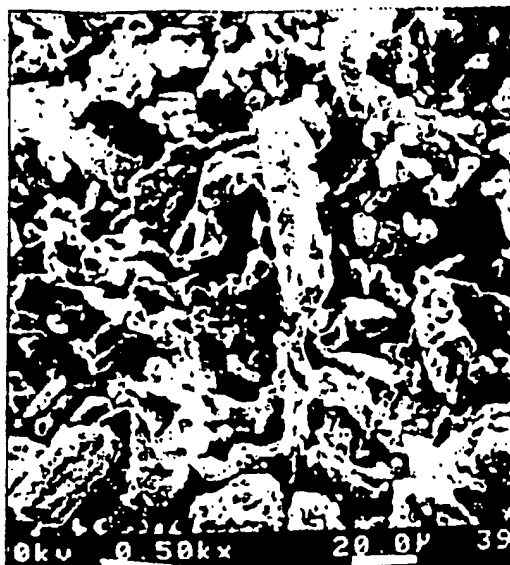
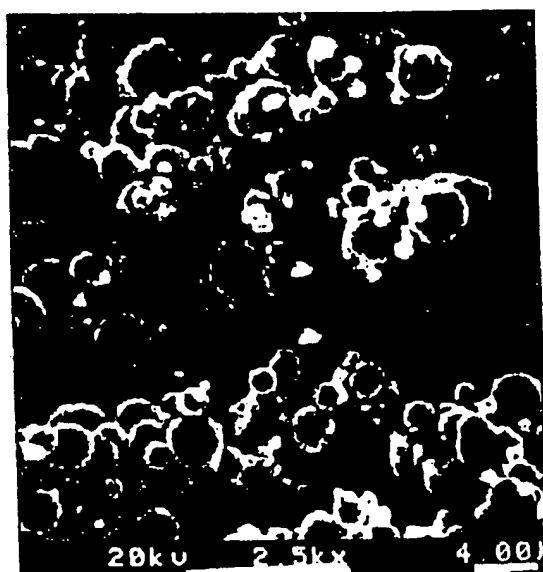


Figure 7

13/34



Titanium



Iron

Figure 8

14/34

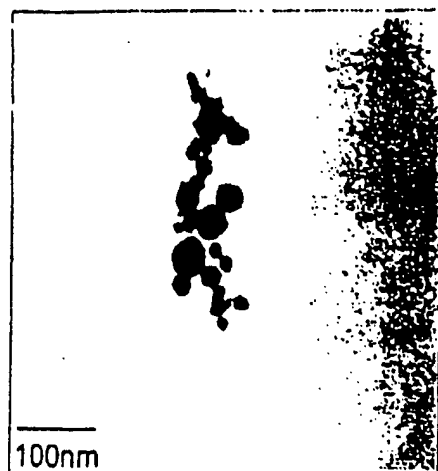


Figure 9

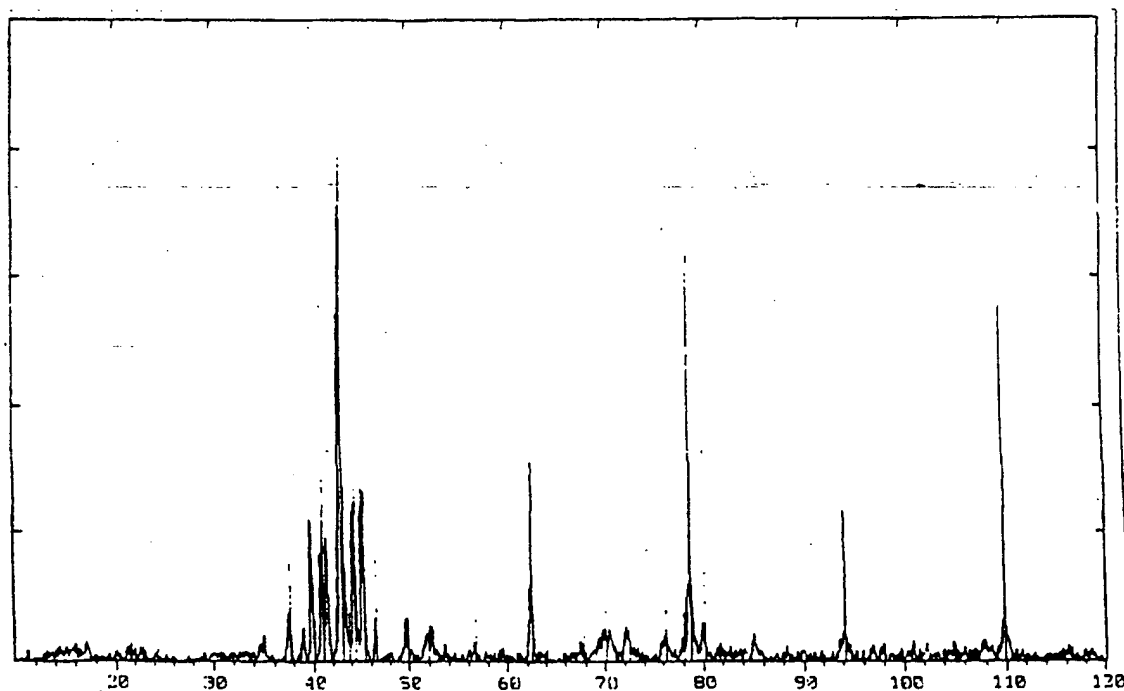


Figure 10

15/34

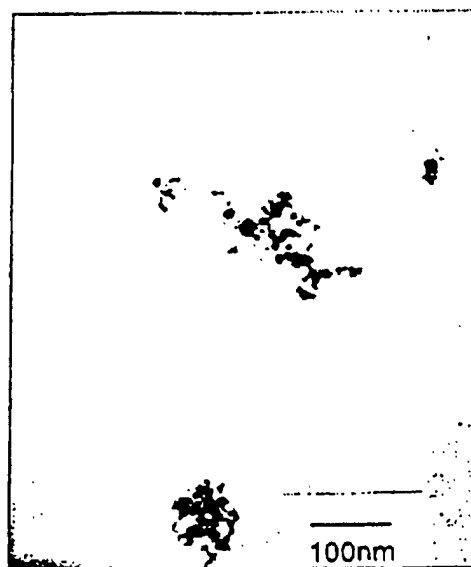


Figure 11

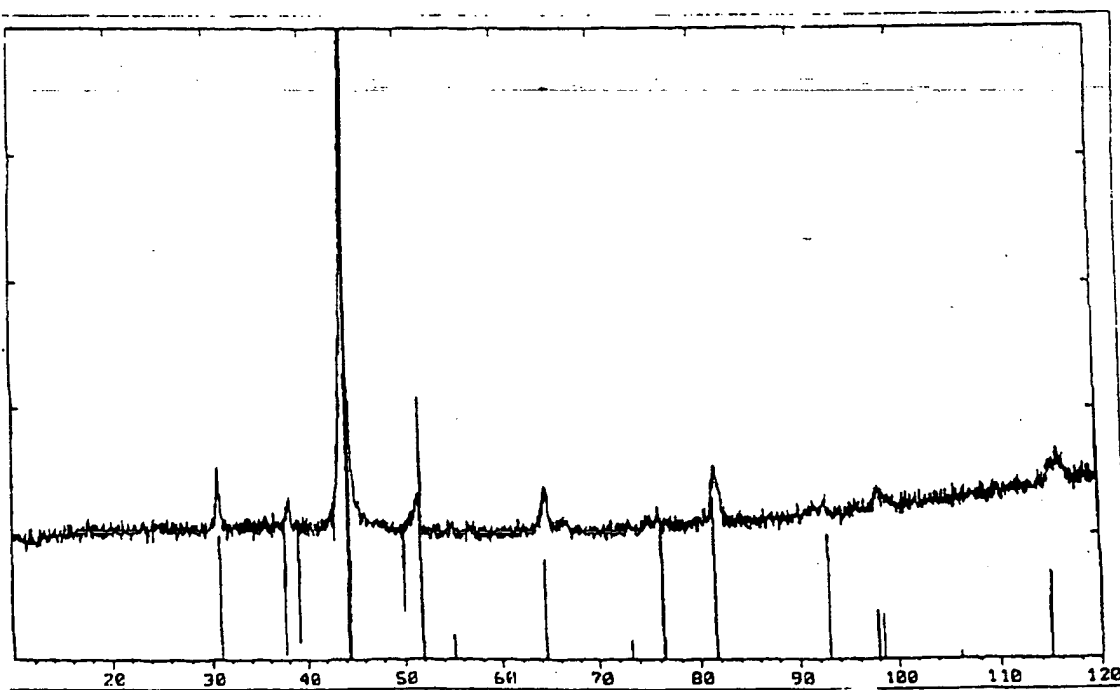


Figure 12

16/34

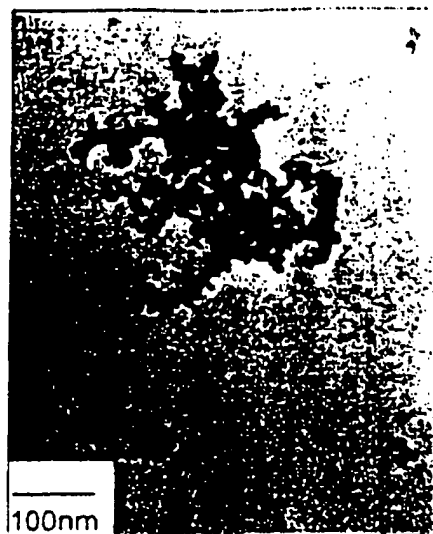


Figure 13

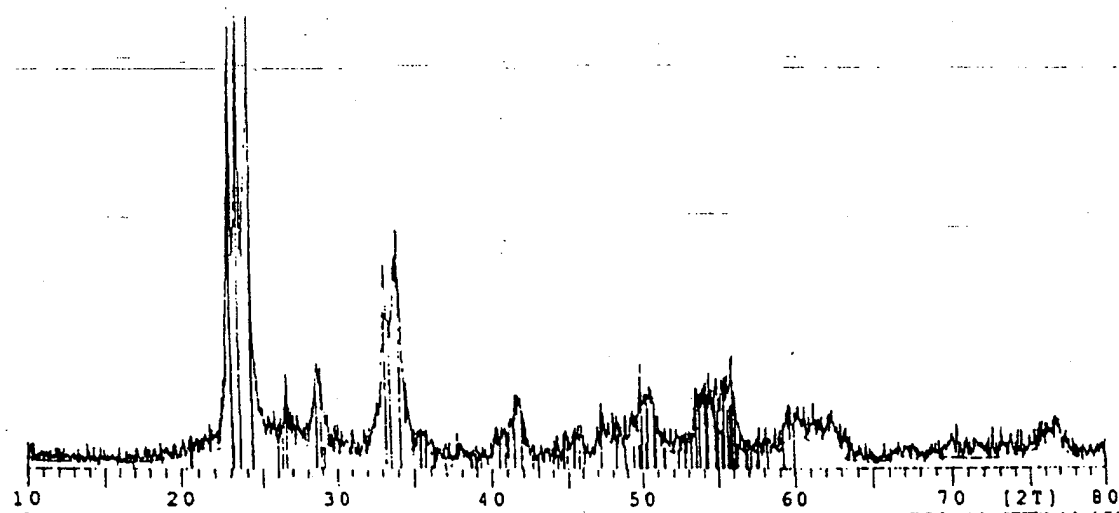


Figure 14

17/34



Figure 15

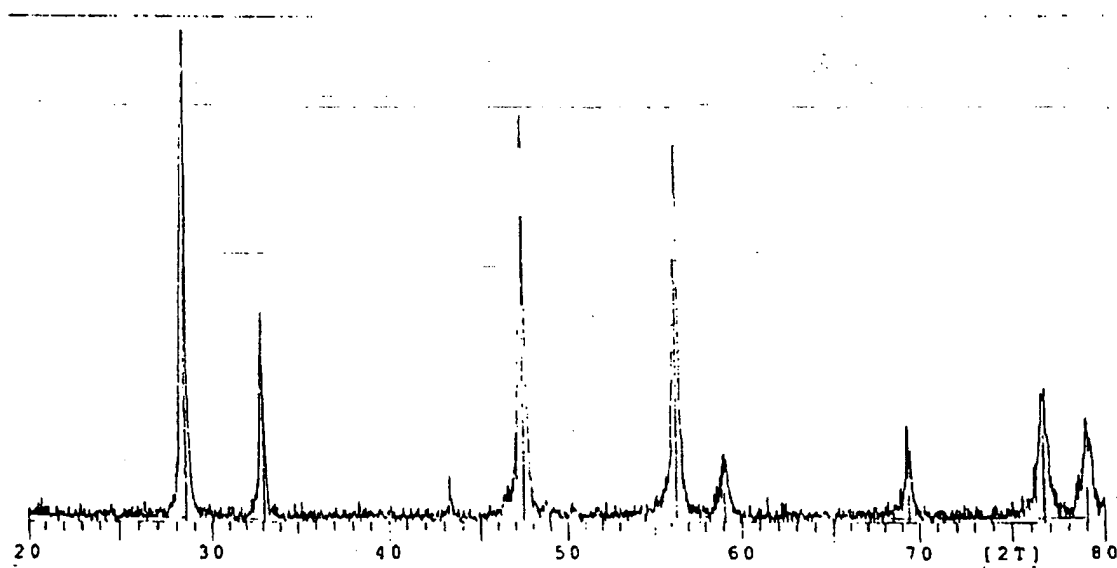


Figure 16

18/34

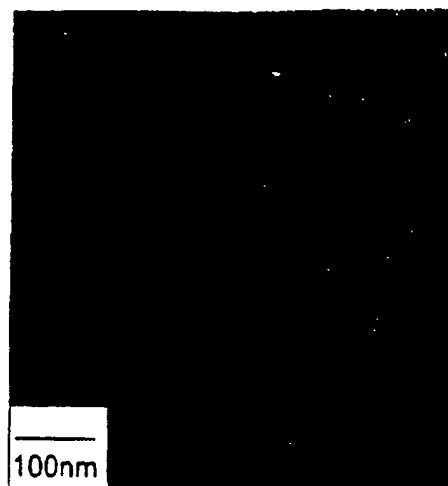


Figure 17



Figure 18

19/34

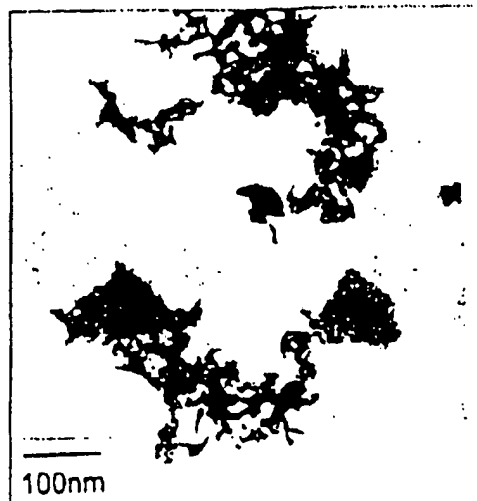


Figure 19

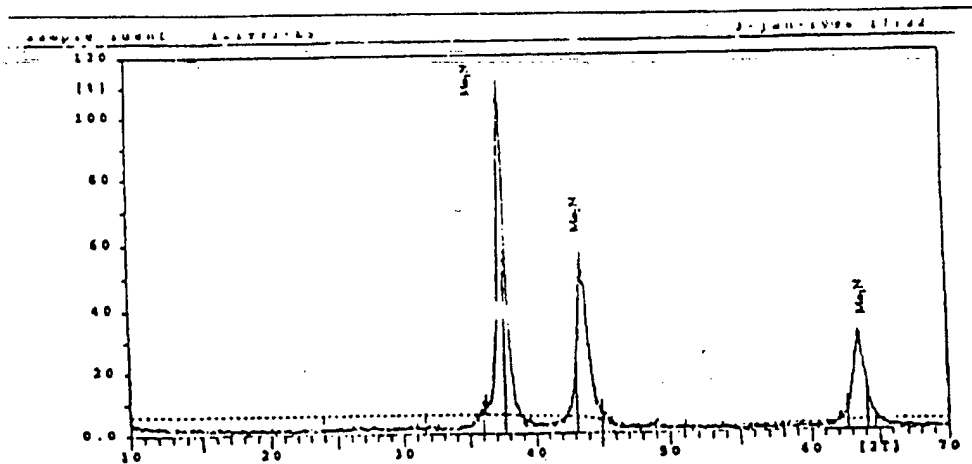


Figure 20

20/34



Figure 21

21/34

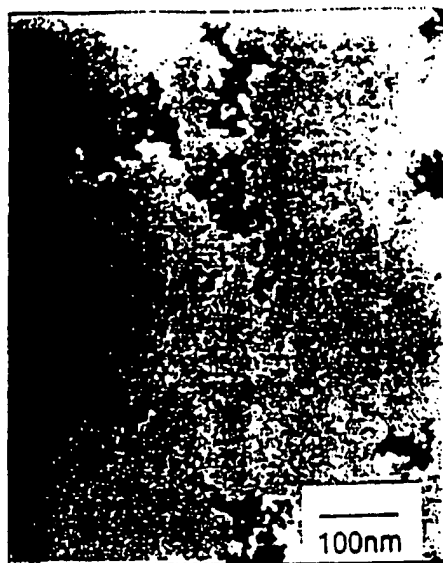


Figure 22

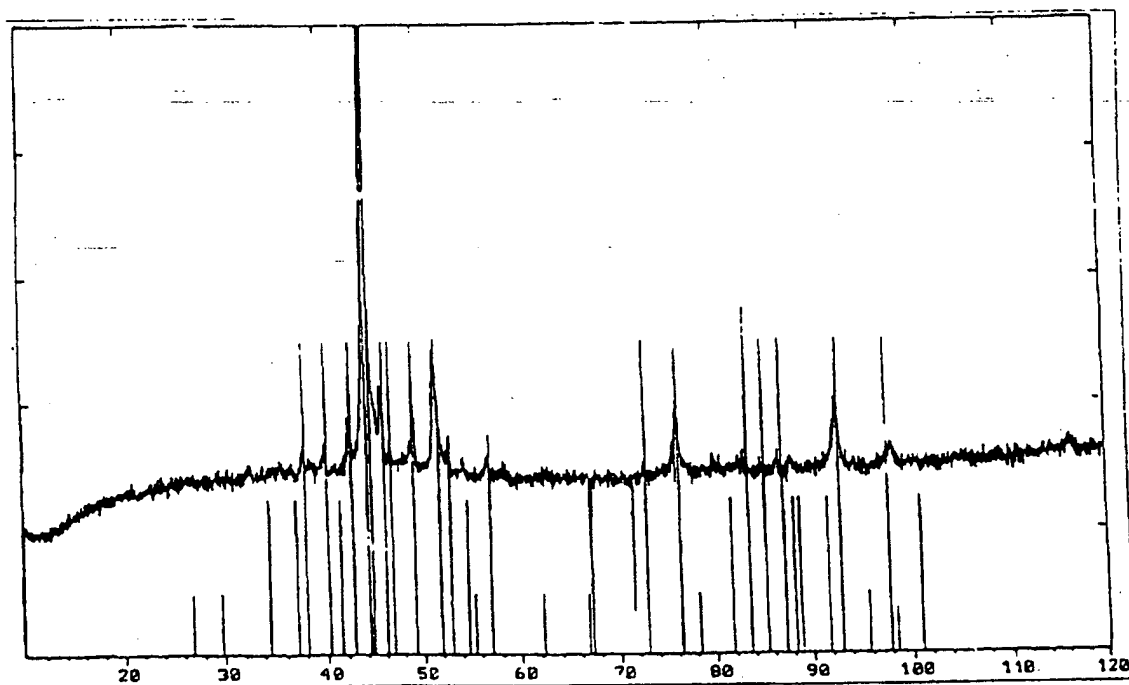


Figure 23

22/34



Figure 24

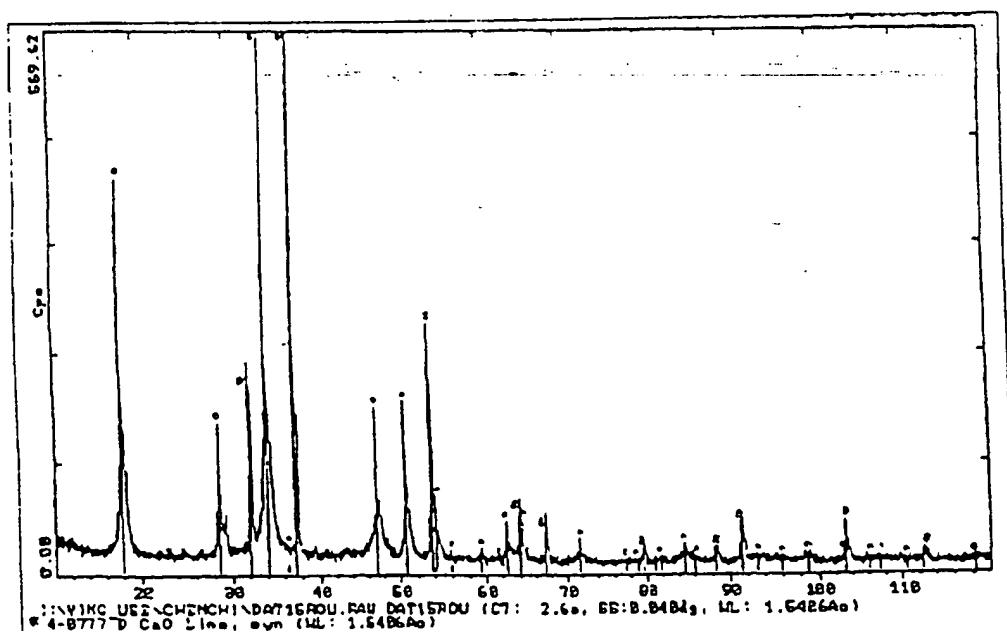


Figure 25

23/34

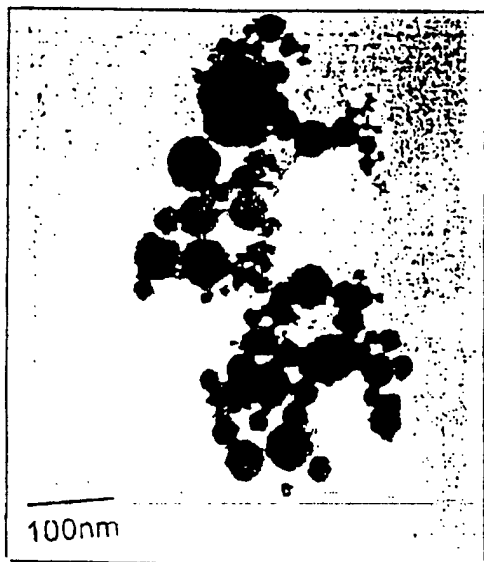


Fig. 26a

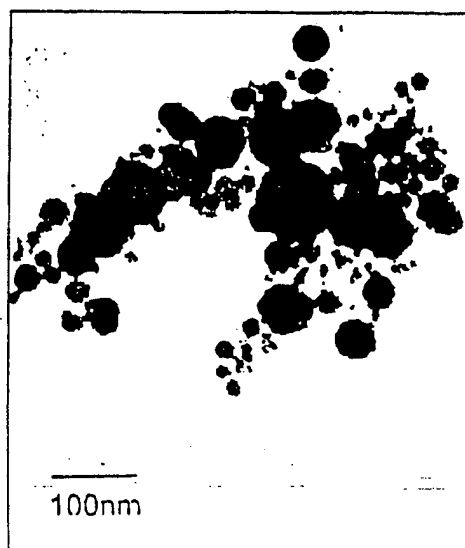
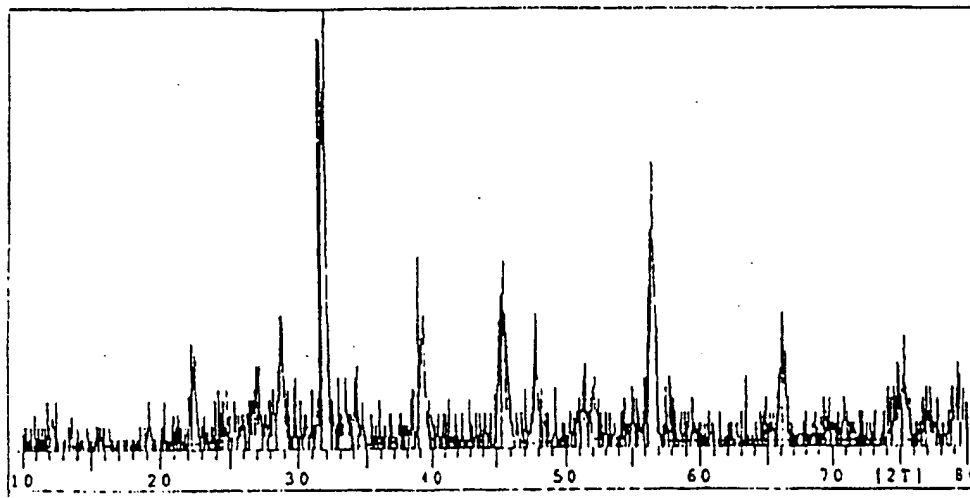


Fig 26 b

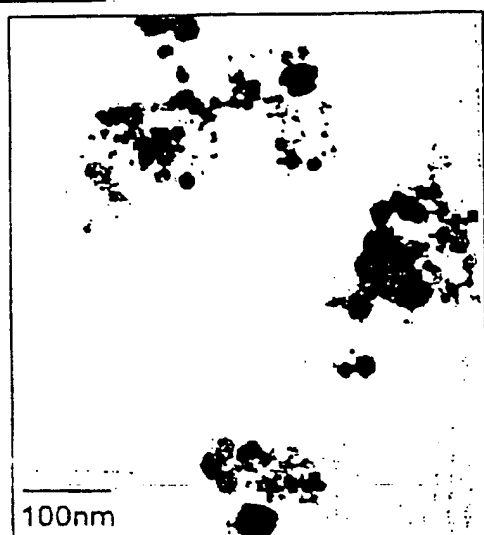
Figures 26a + 26b

24/34



XRD pattern of the powder produced (BaTiO_3). Fig 27

25/34

fig 28a: TEM micrograph of produced SrTiO₃.Fig 28b TEM micrograph of produced SrTiO₃

26/34

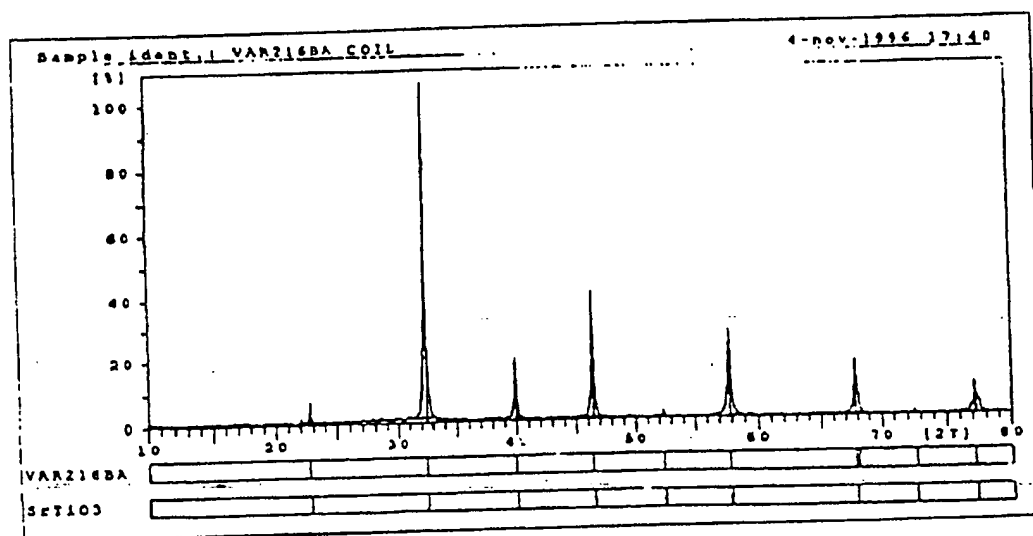
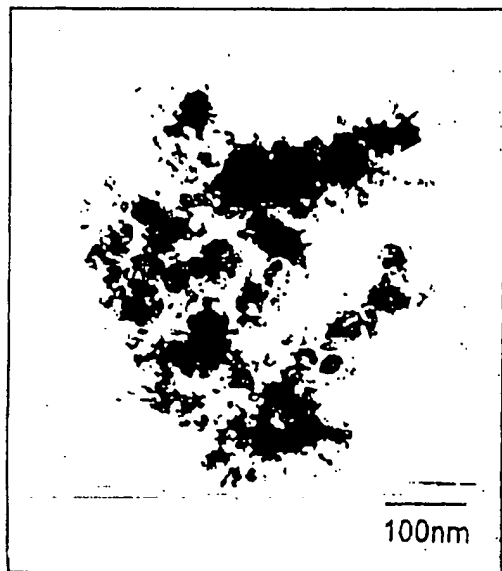


Figure 29. XRD pattern of the powder produced (SrTiO_3).

27/34

Figure 30a TEM micrograph of BaTiO_3 Figure 30b TEM micrograph of BaTiO_3

28/34

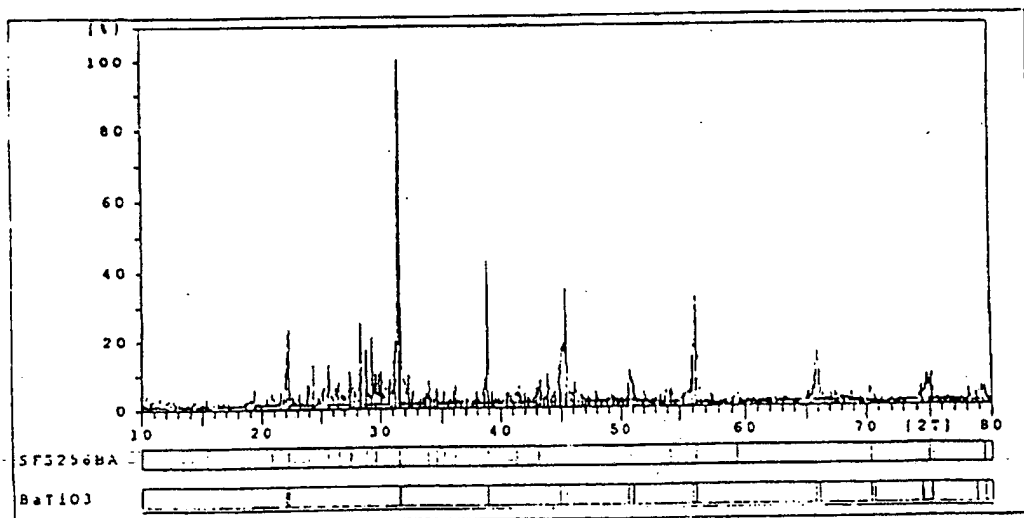


Figure 31: X-ray diffraction pattern of the powder BaTiO_3

29/34

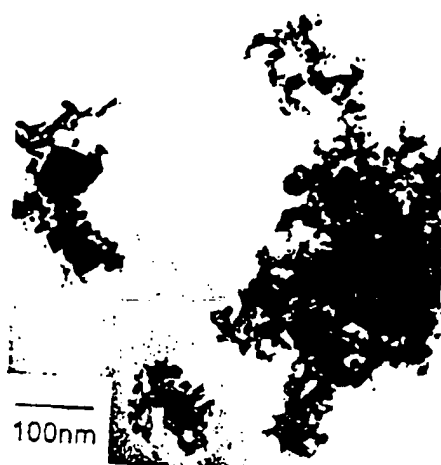


Figure 32: TEM of
Nickel Zinc Ferrite

30/34

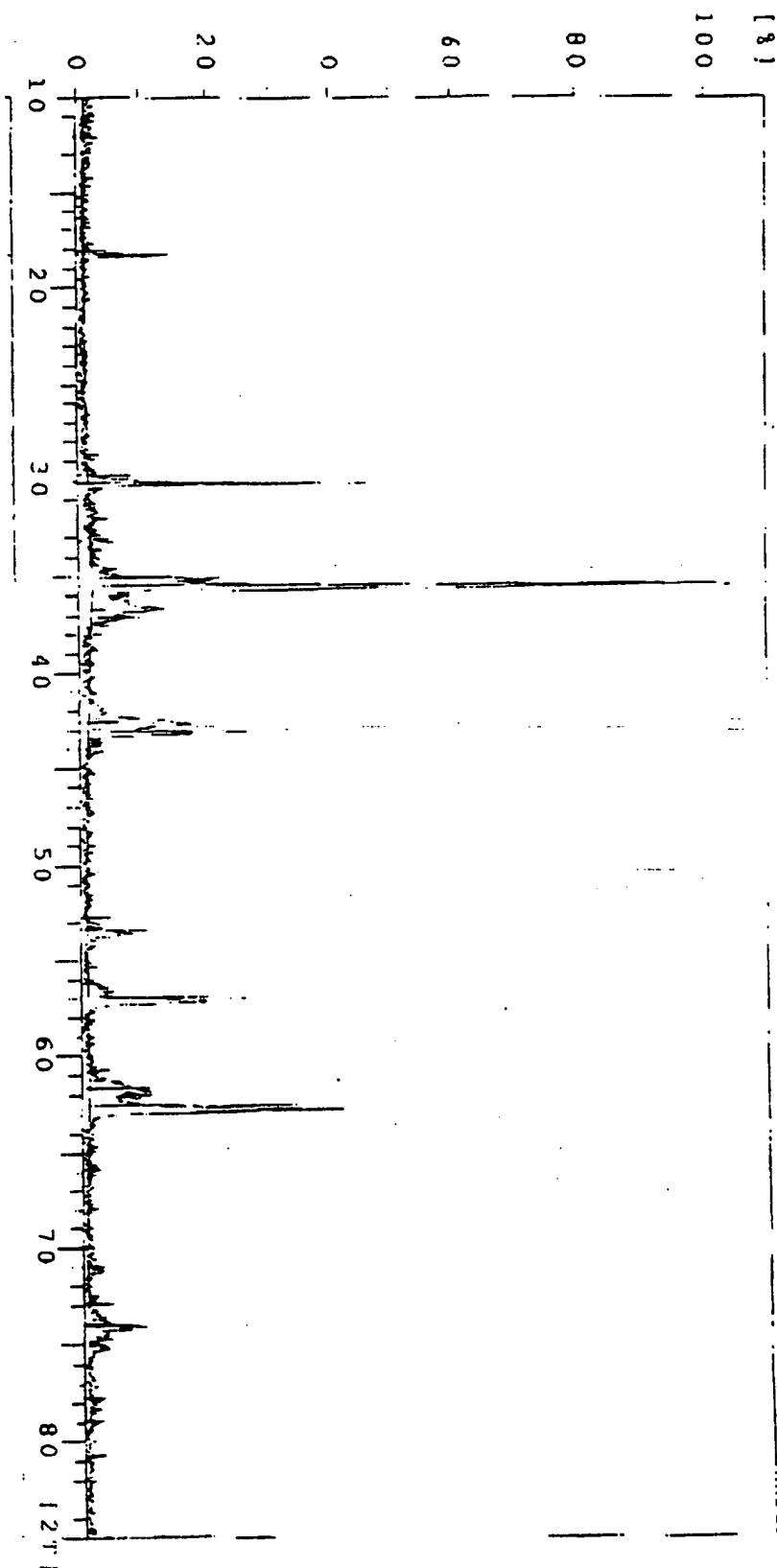


Figure 33: XRD of Nickel Zinc Ferrite

31/34



Fig 34a

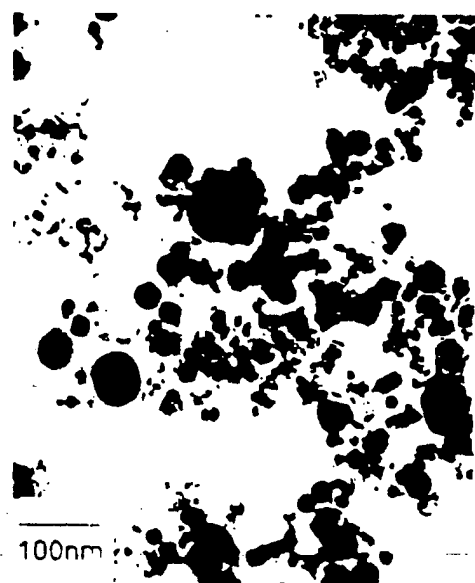


Fig 34b

Figures 34a and 34b
TEM of Ni/Cr/Co/Mo Alloy

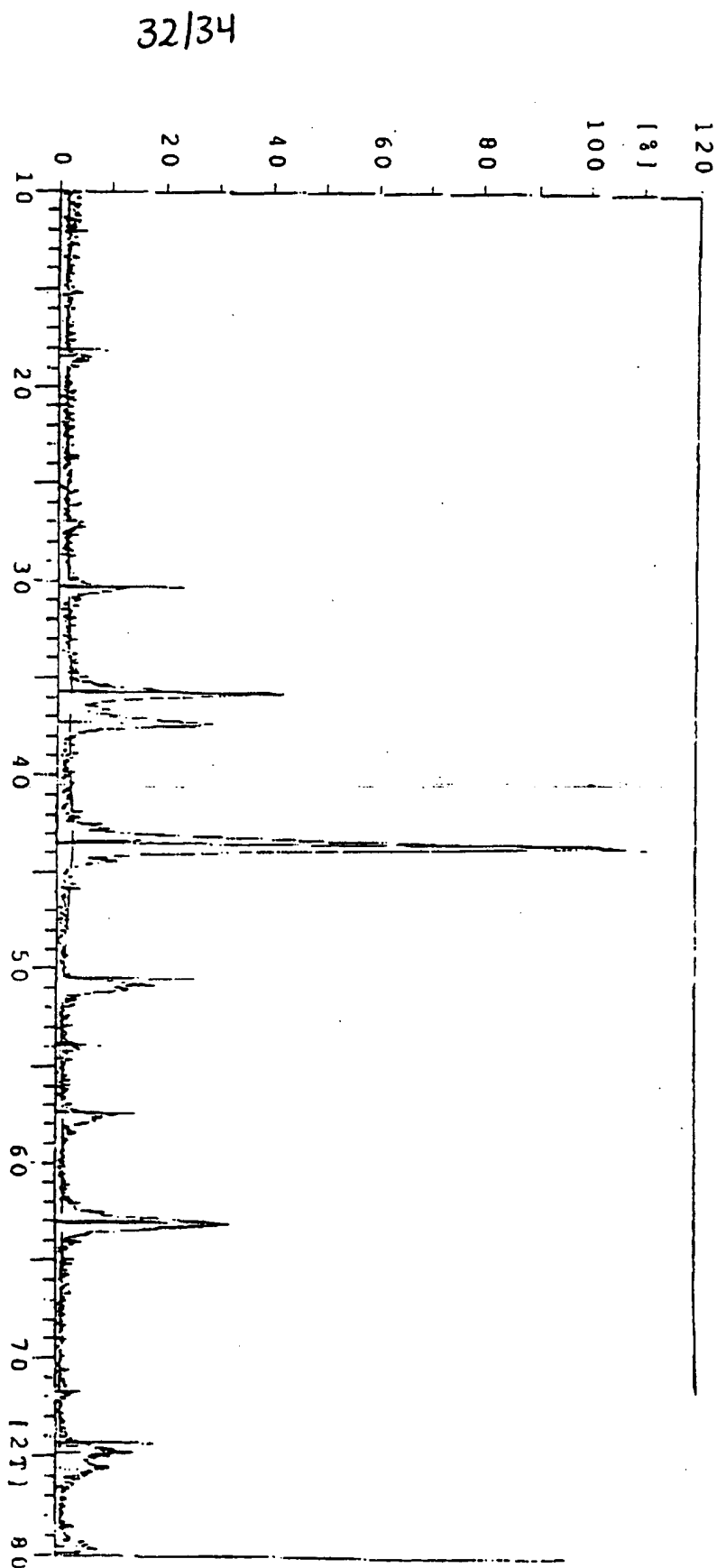
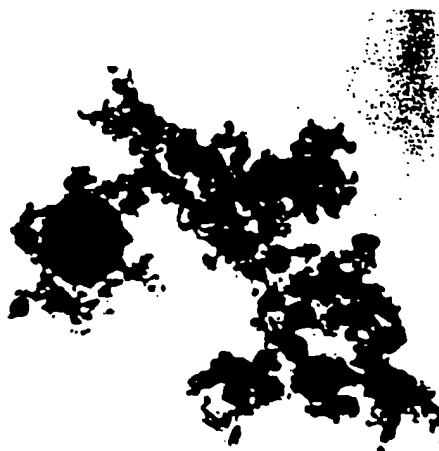


Figure 35:
XRD of Ni/Cr/Ce/Mo Alloy

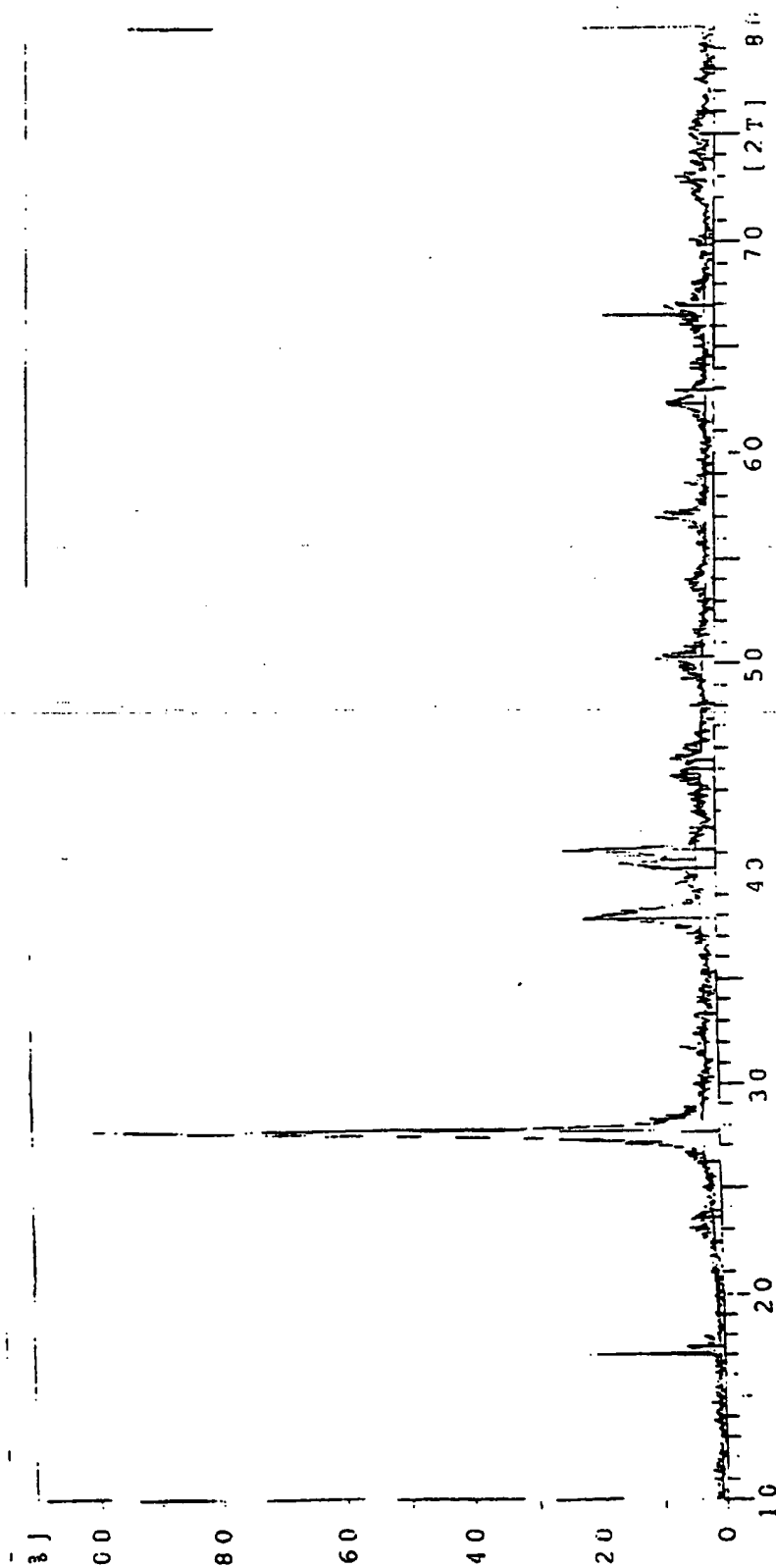
33/34



100nm

Figure 30:
TEM of Bismuth Telluride (Bi_2Te_3)

34/34

Figure 37: XRD of Bismuth Telluride (Bi_2Te_3)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/15463

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B22F9/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 4 851 262 A (MCFEATERS JOHN S) 25 July 1989 see whole document --- -/-- ---	1-4, 6-8, 10-19, 22-42, 45, 46, 49, 50, 53-55, 58-60, 71, 72

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

28 January 1998

Date of mailing of the international search report

04/02/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Riba Vilanova, M

INTERNATIONAL SEARCH REPORT

Intern. Appl. Application No

PCT/US 97/15463

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 484 943 A (MIURA HIROHISA ET AL) 27 November 1984 see whole document	1,2,4, 6-8,10, 11, 13-23, 25-46, 49,50, 53-55, 58-60, 71,72
X	US 4 892 579 A (HAZELTON LOWELL E) 9 January 1990 see whole document	1-23, 25-44
A	US 4 147 534 A (HORI FUMIO) 3 April 1979 see figures see column 3, line 11 - column 9, line 6	1-73
A	GIRARDIN D ET AL: "ULTRAFINE METALLIC POWDERS PREPARED BY HIGH PRESSURE PLASMA: SYNTHESIS AND CHARACTERIZATION" MATERIALS RESEARCH BULLETIN, vol. 25, no. 1, 1 January 1990, pages 119-127, XP000134452 see page 119, line 1 - page 121, line 52	1,4,5, 29,39, 45,46, 49,71

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. onal Application No

PCT/US 97/15463

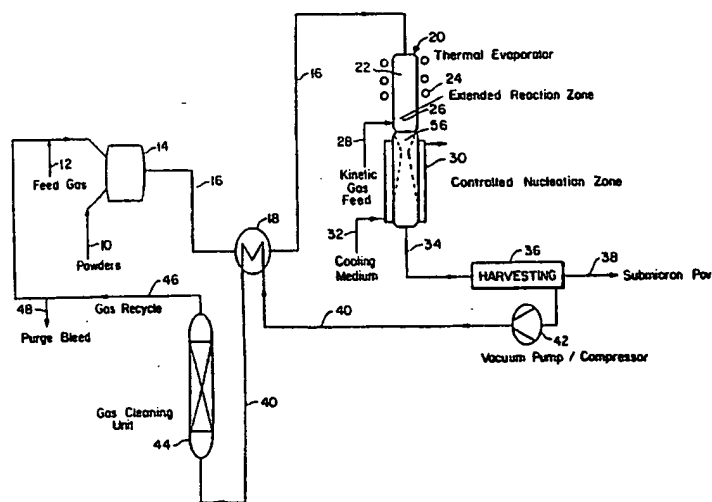
Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4851262 A	25-07-89	AU 590135 B AU 8185287 A	26-10-89 01-12-88
US 4484943 A	27-11-84	JP 1027773 B JP 1543887 C JP 58150427 A JP 1639083 C JP 2055481 B JP 58153532 A JP 1482551 C JP 58153533 A JP 63030963 B EP 0087798 A	30-05-89 15-02-90 07-09-83 31-01-92 27-11-90 12-09-83 27-02-89 12-09-83 21-06-88 07-09-83
US 4892579 A	09-01-90	NONE	
US 4147534 A	03-04-79	JP 1073040 C JP 53022810 A JP 56015697 B AU 503218 B AU 2794077 A CA 1090142 A DE 2736806 A FR 2362214 A GB 1558109 A US 4200264 A	30-11-81 02-03-78 11-04-81 30-08-79 22-02-79 25-11-80 23-02-78 17-03-78 19-12-79 29-04-80



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B22F 9/12	A1	(11) International Publication Number: WO 98/09753 (43) International Publication Date: 12 March 1998 (12.03.98)
(21) International Application Number: PCT/US97/15463 (22) International Filing Date: 3 September 1997 (03.09.97) (30) Priority Data: 08/706,819 3 September 1996 (03.09.96) US 08/707,341 3 September 1996 (03.09.96) US (71) Applicant: NANOMATERIALS RESEARCH CORPORATION [US/US]; 2849 East Elvira Road, Tucson, AZ 85706 (US). (72) Inventors: PIRZADA, Shahid; 6960 N. Avenida Adella, Tucson, AZ 85741 (US). YADAV, Tapesh; 5238 E. Mission Hills, Tucson, AZ 85718 (US). (74) Agent: PASTERNAK, Sam; Choate, Hall & Stewart, Exchange Place, 53 State Street, Boston, MA 02109 (US).	(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	

(54) Title: INTEGRATED THERMAL PROCESS AND APPARATUS FOR THE CONTINUOUS SYNTHESIS OF NANOSCALE POWDERS



(57) Abstract

A continuous process that produces nanoscale powders from different types of precursor material by evaporating the material and quenching the vaporized phase preferably in a converging diverging expansion nozzle. The precursor material suspended in a carrier gas is continuously vaporized at very high temperatures, preferably exceeding 2000 degrees C, and most preferably exceeding 5000 degrees K, in a thermal reaction chamber under conditions that favor nucleation of the resulting vapor. Immediately after the initial nucleation stages, the vapor stream is rapidly and uniformly quenched at rates of at least 1,000 K/sec, preferably above 1,000,000 K/sec, to block the continued growth of the nucleated particles and produce a nanosize powder suspension of narrow particle size distribution. The nanopowder is then harvested by filtration from the quenched vapor stream and the carrier medium is purified, compressed and recycled for mixing with new precursor material in the feed stream.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

INTEGRATED THERMAL PROCESS AND APPARATUS FOR THE CONTINUOUS SYNTHESIS OF NANOSCALE POWDERS

BACKGROUND OF THE INVENTION

5

This invention pertains in general to a process and apparatus for the synthesis of submicron particles. In particular, the invention relates to a novel approach utilizing vaporization and ultra-rapid thermal quenching based on adiabatic expansion of the vapor through a boundary layer converging-diverging nozzle to produce submicron particles under controlled operating conditions.

10

As defined in the art, submicron powders are materials having average grain size below 1 micrometer. Of particular interest are nanoscale powders; namely, submicron powders with grain size less than 100 nanometers and with a significant fraction of interfacial atoms. Of great interest are powders with grain size of less than 50 nanometers. Of greater interest are powders with grain size less than 20 nanometers. Of greatest interest are powders with grain size less than 10 nanometers. It is known that within these size ranges a variety of confinement effects occur that dramatically change the properties of the material. A property will be altered when the entity or mechanism responsible for that property is confined within a space smaller than some critical length associated with that entity or mechanism. See H. Gleiter, Mechanical Properties and Deformation Behavior of Materials Having Ultra-Fine Microstructures, Nastasi et al. Ed., 3-35 (1993); and R. W. Siegel, Mechanical Properties and Deformation Behavior of Materials Having Ultra-fine Microstructures, Nastasi et al. Ed., 509 (1993), which are included herein by reference. Such confinement effects can, therefore lead to a wide range of commercially important properties. For example, a normally ductile metal will become significantly harder if its grain size is reduced to the point where moving dislocations through its crystal lattice are no longer able to occur at normal levels of applied stress. Since the stress required to produce a Frank-Read dislocation is inversely proportional to the spacing between its pinning points, as one skilled in the art would readily understand, a critical length in this case is that for which the stress necessary to produce a dislocation becomes larger than the conventional yield stress for the given metal.

20

25

30

Thus, confinement effects can be exploited to produce extremely hard and strong materials with much higher yield stress than exhibited by the conventional form of their precursors. See Nieman et al., "Mechanical Behavior of Nanocrystalline Cu and Pd," J. Mater. Res., 6, 1012 (1991); and Nieman et al., "Tensile Strength and Creep Properties of Nanocrystalline Palladium," Scripta Metall. et Mater., 24, 145 (1990), which are included herein by reference. The same principle has also been used to manufacture unique optical materials with grain sizes tailored for excitonic interactions with particular wavelengths, Skandon et al., "Nanostructured Y_2O_3 : Synthesis and Relation to Microstructure and Properties," Scripta Metall. et Mater., 25, 2389 (1991); electroceramics with unique electronic and electrical characteristics, Eastman et al., "Processing and Properties of Nanophase Oxides," Mater. Res. Soc. Symp. Proc., 155, 255 (1989); superplastic ceramics with grain sizes engineered to allow low cost, rapid net-shape forming of ceramics as a substitute process for machining of ceramics, H. Hahn et al., "Low Temperature Sintering and Deformation of Nanocrystalline TiO_2 ," Mater. Res. Soc. Symp. Proc., 196, 71 (1990) and M. J. Mayo, Mechanical Properties and Deformation Behavior of Materials Having Ultra-fine Microstructures, Nastasi et al. Ed., 361 (1993); catalysts with extremely high surface areas, high selectivity and activity, Beck and Siegel, "The Dissociative Adsorption of Hydrogen Sulfide over Nanophase Titanium Dioxide," J. Mater. Res., 7, 2840 (1992); materials with unique electrochemical properties, Tamaki et al., "Grain-Size Effects in Tungsten Oxide-Based Sensor for Nitrogen Oxides," J. Electrochem. Soc., 141, 2207 (1994); and materials that exhibit unprecedented magnetic properties, Sugaya et al., "Soft Magnetic Properties of Nanostructure-Controlled Magnetic Materials," IEEE Trans. on Magnetics, 31, 2197 (1995) and C.E. Yeack-Scranton, Nanomagnetism, Kluwer Academic, Netherland, 1-6 (1993), all of which are included herein by reference. Quantum confined and nanometer cluster materials, therefore, are an extraordinary opportunity for design, development and commercialization of a wide range of structural, electrochemical, electrical, optical, electronic, magnetic and chemical applications. Furthermore, since they represent a whole new family of material precursors where conventional coarse-grain physiochemical mechanisms are not applicable, these materials offer a unique

combination of properties that can enable novel and multifunctional components of unmatched performance.

Although this opportunity has been apparent for several years, large scale commercialization has remained unrealized because of the high cost and low throughput of existing processes for producing nanopowders, the current lack of process control over size and size distribution of the resulting material, the unpredictable composition of its constituent phases, and the lack of control over the nature of and the interactions among the interfaces created between the constituent phases. Nanopowders may indeed represent the threshold of a new era in materials technology, but the key to their full utilization depends on the development of new processes for producing nanopowders economically and in commercially viable quantities under controlled operating conditions.

In recent years, several methods have been used for producing nanopowders and the materials produced by this prior-art technology have confirmed the fact that nanopowders possess important technical properties that show the potential for becoming commercially significant. However, all known production methods consist of batch processes that are too expensive to yield commercially affordable materials for bulk applications (current production costs for these processes are orders of magnitude higher than the \$10.00/lb target price considered economical for bulk applications of these materials). Therefore, the commercial future of nanopowders depends on the development of a process that can produce nanopowders with predetermined properties, in commercially viable quantities, and at an affordable cost.

An additional and significant problem encountered by the performance ceramics industry is the use of environmentally undesirable solvents and additives (acids, alkalis, ammonia and aromatic dispersants to name a few examples) in large quantities. Unfortunately, the present processing techniques continue to require the use of solvents and additives and the anticipated growth in this market for ceramic devices suggests that this environmental hazard will only increase.

Ideally, the synthesis and processing technology for nanopowders should allow control of the size and size distribution of the constituent structures and phases (this is critical to the mechanistic performance of nanopowders); allow control of the composition of the phases in the nanomaterial (critical to define the property domain

of the nanomaterial); allow control over the nature of interfaces (e.g. purity) and the interaction between interfaces (critical to the interface-based characteristics of the nanopowders); and minimize the use of environmentally undesirable solvents and additives. None of the known processes for the synthesis of nanomaterials possesses these characteristics; therefore, none is suitable for bulk commercialization of nanopowders.

In particular, prior-art processes are all batch, and have high energy or solvent processing requirements, which are all inherent limitations to the cost-effective and large-scale production of nanopowders. The processes currently in use can be classified into three general groups: chemical, mechanical-attrition, and gas-condensation methods. The chemical methods include precipitation techniques, sol-gel processes, and inverse-micelle methods. See Beck and Siegel, "The Dissociative Adsorption of Hydrogen Sulfide over Nanophase Titanium Dioxide," J. Mater. Res., 7, 2840 (1992), and Steigerwald and Brus, "Synthesis, Stabilization, and Electronic Structure of Quantum Semiconductor Nanoclusters," 11 Ann. Rev. Mater. Sci., 191 471 (1989), which are included herein by reference. These processes have been used to successfully synthesize narrowly distributed nanopowders; however, being chemical-media based, the resulting nanopowders are covered with chemical surface layers. This surface covering adversely affects the properties of the nanopowders and inhibits their further processing into bulk materials. In addition, the use of solvents and chemicals has a significant economic impact on the synthesis process because of the costs of chemicals and, as discussed above, the pollution remediation required by their use.

The mechanical attrition methods rely on the physical decomposition of coarser grains through severe mechanical deformation. Such processing methods are energy intensive, have low flexibility, are susceptible to contamination by attrition tools or media, and afford little control over the quality and consistency of the final product.

The gas condensation methods essentially involve the evaporation of a coarse (at least micron size) source of precursor material, such as a metal, inorganic, etc., in an inert gas at a low pressure. The evaporated source atoms or molecules collide with the gas atoms or molecules and lose energy, thereby causing a homogeneous

condensation of atom or molecule clusters in the supersaturated vicinity of the precursor source. The further accretion and/or coalescence of the nucleated particles is minimized by rapid removal of the nanometer-sized powders so formed from the region of supersaturation. See R. Uyeda, "Studies of Ultrafine Particles in Japan: Crystallography, Methods of Preparation and Technological Applications," 11 Prog. Mater. Sci., 35, 1 (1991), and R. W. Siegel, Materials Science and Technology, 15, VCH, Weinheim, 583 (1991), which are incorporated herein by reference.

Alternatively, gas condensation processes may involve gas-phase reactions. Some of the known gas condensation processes have produced nanomaterials of acceptable size distribution, but they are all batch operations and are not readily scaleable for commercial exploitation.

Additionally, rapid solidification processing of high temperature liquids and vapors has been extensively researched. See Loren A. Jacobson and J. McKittrick, "Rapid Solidification Processing", Materials Sciences & Eng., R-11, 355-408 (1994), which is incorporated herein by reference. Such process techniques are used to prepare fine microstructures (micron sized), increase solid solubility of alloy elements, and prepare non-equilibrium phases, particularly in powder metallurgy. Conventional rapid solidification methods, such as oil quench, gas quench, chill casting, and centrifugal atomization, achieve thermal quench rates of 10^2 to 10^5 K/sec.

Higher quench rates are very desirable because they can enable the synthesis of powders that are submicron in domain size and, at rates greater than 10^6 K/sec, can enable the synthesis of powders with domain size less than 100 nanometers. As defined in the art, submicron powders are materials having average grain size below 1 micrometer. Of particular interest are nanoscale powders; namely, submicron powders with grain size less than 100 nanometers. Finer domain sizes are desirable because the physiochemical properties of materials are remarkably different and commercially useful when the domain size is reduced below 100 nanometers. Nanoscale powders also exhibit very high surface areas and enhanced surface activity for physical and chemical reactions.

To achieve higher cooling rates, contact quenching methods such as splat cooling and glazing have been suggested. See Jones, "Splat Cooling and Metastable

Phases," Rep. Progr. Phys., 36, 1425 (1973), which is incorporated herein by reference. However, these methods are not suitable for thermal quenching of high temperature vapors (greater than 1500 K) because these temperatures lead to thermokinetic transformations from reactions at contact surfaces. These methods are also not useful for high temperature vapors of materials such as carbides, nitride, refractory metals, alloys, and multiphase nonequilibrium phases because the high temperatures can irreversibly damage the contact surfaces. Furthermore, these prior-art methods are not suited for thermally quenching high temperature, chemically-active vapors (such as those resulting from chemical reactions between feed components at high temperatures).

U. S. Patents 5,407,458, 5,403,375, 5,384,306, and 5,389,585 by König et al. all describe the production of nanoscale powders using a process of the reaction of chemically active vapors between feed components at high temperatures. The corresponding metal compounds and corresponding reactants are reacted in the gas phase in a reactor at a temperature of 2000 degrees C or lower, homogeneously condensed directly from the gas phase in the absence of any wall reactions and subsequently removed from the reaction medium. It is asserted that, by separately preheating the process gases to at least the reaction temperature, the nucleation site can be confined. A flow optimized hot wall reactor is used as the source because it is believed by König et al that other sources such as a plasma flame or laser beam result in uncontrollable reaction conditions prevailing in various parts of the reaction zone with very steep temperature gradients and/or turbulent flow conditions, resulting in the powders having broad particle size distribution. The nozzle in the König et al. process relates to feed system of the process and does not mechanistically participate with the evaporation, reactions, condensation or growth of fine powders. Most notably, because the process described by König et al. is a reactive process, byproducts such as HCl are formed, which ultimately affect the purity of the nanomaterials. Because their temperature is limited to 2000 degrees, the process is limited to precursors that have a vaporization temperature less than 2000 degrees C. In addition, König et al. teach a laminar flow technique that would face scale up limitations. This is so because the powder characteristics are related to residence time of gases in the reactor, which in turn is related to the parabolic flow associated with

laminar flow. In other words, in the König et al. process, there is a radially varying profile in residence time (the gas at the center is moving faster than the gas near the wall). As the reactor is scaled up, the powder size will get more broad in distribution.

5 Therefore, there continues to be a need for a low-cost process (less than \$10/lb) that is suitable for large-scale production of nanopowders under controlled operating conditions. The present invention discloses a pioneering and unique thermal condensation process. This process can be a strictly physical process which starts with a material, vaporizes it at very high temperatures (above 2000 degrees C),
10 then very rapidly recondenses it to produce nanoscale powders, thus eliminating the formation of undesirable byproducts. This process satisfies these requirements for the continuous production of nanopowders in bulk quantities, and additionally discloses a Joule-Thompson nozzle that is particularly suited for ultra-rapid quenching and condensation of vaporized material described above.

15

SUMMARY OF THE INVENTION

One of the objectives of this invention is a low capital-cost process for the production of quantum confined and nanometer cluster materials of various inorganic
20 compositions including but not limited to carbides, nitrides, oxides, chalcogenides, halogenides, alloys, metals, complex compositions, and composites in bulk quantities.

Another objective of this invention is to develop techniques to control the size, shape,
25 surface area, morphology, surface characteristics, surface composition, distribution, and degree of agglomeration.

Another objective of the invention is a device that enables very high quench rates of high temperature vapors that can produce nanoscale powders.

30

Yet another objective of this invention is to develop a method of preventing the deposition of the quantum confined and nanometer cluster materials on the walls of the process equipment.

- 5 Another objective is to develop a process which allows vaporization of ingredients at very high temperatures (> 2000 degrees C) yet permits quenching at very high rates.

Yet another objective is to develop a process which produces product but generates no byproduct.

10

A further objective of this invention is to develop a method of ensuring high yield and high selectivity, including but not limited to harvesting 95% + of the quantum confined and nanometer cluster material produced.

- 15 Yet another objective of this invention is to prevent the damage of the quantum confined and nanometer cluster materials during and after their synthesis.

Another objective is a device that is simple, easy to operate, and flexible with respect to operating parameters, so as to allow the production of multiple products.

20

Another objective is a device that prevents contamination of the quenched product from the materials of construction used for the quench equipment.

- 25 Yet another objective is a device that allows flexibility in the composition of the vapor quenched, in quench rates and quench volume.

Another objective of the invention is a process and device that can be carried out with low utility costs (that is, low energy input, energy output, and maintenance expenses).

- 30 Another objective is a process and device with low operating costs (i.e., labor, recycling, raw materials, plant space, etc.); accordingly, the invention aims at a process and device with high yield per pass and high product selectivity.

Another objective is a process that is continuous and suitable for scaling up to production rates in the order of tons per day.

Yet another objective is a process that is simple, easy to operate, and flexible, so as to
5 allow the production of multiple products with relatively simple operating changes.

Still another objective is a process and device that are safe and environmentally benign.

10 Finally, another objective is an operationally stable process that requires a minimal external-control structure for steady-state operation.

A process that satisfies most of these features would be very desirable because it would enable the economical manufacture of nanopowders in bulk quantities.
15 Therefore, according to the foregoing objectives, one aspect of the this invention involves the continuous vaporization at very high temperatures of commercially-available, coarse precursor material suspended in a carrier gas in a thermal reaction chamber under conditions that minimize superheating and favor nucleation of the resulting vapor. Optionally, a kinetic gas feed may be mixed with the vapor in the
20 reactor to reach a thermokinetic state of the vapor that may be required to produce controlled nucleation of solid powders from the vapor stream. Immediately after the initial nucleation stages, the vapor stream is rapidly and uniformly quenched at rates of at least 1,000 K per second, preferably greater than 1,000,000 K per second, to block the continued growth of the nucleated particles and produce a nanosize powder
25 suspension of narrow particle-size distribution. The nanopowder is then harvested by filtration from the quenched vapor stream and the carrier medium is purified, compressed and recycled for mixing with new precursor material in the feed stream.

According to another aspect of the invention, the thermal quenching is carried out in a converging-diverging expansion nozzle that exploits the Joule-Thompson
30 principle of adiabatic expansion of high-temperature vapors. Since the physical characteristics of the nozzle determine the extent of cooling, pressure drop and density drop, the condensation process can be advantageously controlled by utilizing

a nozzle of predetermined key dimensions to fit the requirements of the material being condensed.

Various other purposes and advantages of the invention will become clear from its description in the specification that follows and from the novel features particularly pointed out in the appended claims. Therefore, to the accomplishment of the objectives described above, this invention consists of the features hereinafter illustrated in the drawings, fully described in the detailed description of the preferred embodiments and particularly pointed out in the claims. However, such drawings and description disclose only some of the various ways in which the invention may be practiced.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic representation of the adiabatic-expansion, thermal quenching process of the present invention.

5

Figure 2a is a sketch of a converging-diverging nozzle illustrating the relationship between critical parameters of the process and of the nozzle used to carry out the invention.

10 Figure 2b is a sketch of a converging-diverging nozzle illustrating the key design parameters of the device.

Figure 3a, 3b and 3c are cross-sectional elevational, top, and cross-sectional elevational drawings, respectively of a converging-diverging, adiabatic expansion
15 nozzle according to the preferred embodiment of the invention.

Figure 4 is a schematic illustration of a pilot-plant process according to the preferred embodiment of the invention.

20 Figures 5a, 5b, 5c, and 5d are drawings of the preferred embodiment of the present invention for a scaled up process.

Figure 6 is the transmission electron micrograph of the zinc nanosize powder produced by the invention.

25

Figure 7 is an X-ray diffraction patterns of the product of Example 1, indicating that the only phase present was zinc.

Figure 8 is a SEM micrograph of the feed powders iron and titanium used, showing
30 that they were greater than 1 micrometer when fed.

Figure 9 is a transmission electron microscope image of the iron-titanium alloy nanopowders produced in Example 2, showing them to be in the 10-45 nanometer range.

- 5 Figure 10 is an X-ray diffraction pattern of the product of Example 2, indicating that the phases formed were titanium, iron and iron-titanium intermetallic.

Figure 11 is a transmission electron microscope image of the nickel aluminide nanopowder produced in Example 3.

10

Figure 12 is an X-ray diffraction pattern of the product of Example 3, indicating that the phase formed was NiAl.

- Figure 13 is a transmission electron microscope image of the tungsten oxide
15 nanopowder produced in Example 4.

Figure 14 is an X-ray diffraction pattern of the product of Example 4, indicating that the phase formed was WO_3 .

- 20 Figure 15 is a transmission electron microscope image of the cerium oxide nanopowder produced in Example 5.

Figure 16 is an X-ray diffraction pattern of the product of Example 5, indicating that the phase formed was CeO_2 .

25

Figure 17 is a transmission electron microscope image of the silicon carbide nanopowder produced in Example 6.

- Figure 18 is an X-ray diffraction pattern of the product of Example 6, indicating that
30 the phase formed was SiC.

Figure 19 is a transmission electron microscope image of the molybdenum nitride nanopowder produced in Example 7.

Figure 20 is an X-ray diffraction pattern of the product of Example 7, indicating that
5 the phase formed was Mo_2N .

Figure 21 is a scanning electron microscope image of the nickel boride ceramic used in Example 8, showing that the feed powder was greater than 1 micrometer.

10 Figure 22 is a transmission electron microscope image of the Ni and Ni_3B nanopowders produced in Example 8, showing them to be in the 10-30 nanometer range.

Figure 23 is an X-ray diffraction pattern of the product of Example 8, indicating that
15 the phases formed were Ni and Ni_3B .

Figure 24 is a transmission electron microscope image of the calcium-oxide nanopowders produced in Example 9, showing them to be in the 5-20 nanometer range.

20

Figure 25 is an X-ray diffraction pattern of the product of Example 9, indicating that the phase formed was CaO .

Figures 26a and 26b are transmission electron microscope micrographs of barium titanate produced in Example 10.
25

Figure 27 is an X-ray diffraction pattern of barium titanate produced in Example 10.

Figures 28a and 28b are transmission electron microscope micrographs of strontium titanate produced in Example 10.
30

Figure 29 is an X-ray diffraction pattern of strontium titanate produced in Example 10.

5 Figures 30a and 30b are transmission electron microscope micrographs of barium titanate produced in Example 10.

Figure 31 is an X-ray diffraction pattern of barium titanate produced in Example 10.

10 Figure 32 is a transmission electron microscope micrograph of nickel zinc ferrite produced in Example 11.

Figure 33 is an X-ray diffraction pattern of nickel zinc ferrite produced in Example 11.

15 Figures 34a and 34b are transmission electron micrographs of Ni/Cr/Co/Mo alloy produced in Example 12.

Figure 35 is an X-ray diffraction pattern of Ni/Cr/Co/Mo alloy produced in Example 12.

20

Figure 36 is a transmission electron micrograph of bismuth telluride produced in Example 13.

Figure 37 is an X-ray diffraction pattern of bismuth telluride produced in Example 13.

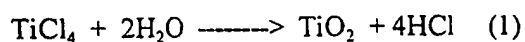
25

DETAILED DESCRIPTION OF THE INVENTION

A primary aspect of this invention lies in the discovery that the size and size distribution of nanopowders produced by vapor condensation can be controlled by interrupting the growth process through ultra-rapid thermal quenching of the condensing vapor. Another critical aspect of the invention is the realization that Joule-Thompson adiabatic expansion provides a controllable process for quenching such condensing vapor at predetermined rates as high as 10^6 °C/sec, or greater, as required for producing nanopowders of desired properties. A third, important aspect of the invention is the development of a converging-diverging nozzle to implement the adiabatic expansion process of the invention under predictable conditions for a variety of precursor materials and operating conditions.

Referring to the drawings, wherein like parts are designated throughout with like numerals and symbols, Fig. 1 shows the process flow diagram and a schematic representation of the apparatus of the invention as applied to solid precursors, such as metals, alloys, ceramics, composites, and combinations thereof. It is understood that the process applies equivalently to other forms of precursors such as liquid, gaseous, slurry, and combinations thereof. A feed stream 10 of such a precursor material in powder form is premixed with a feed gas stream 12 (such as argon, helium, nitrogen, oxygen, hydrogen, water vapor, methane, air, or a combination thereof, depending on the particular precursor being processed and the corresponding atmosphere - inert, oxidizing, or reducing - required for the process) in mixing apparatus 14 appropriate to create a suspension. It is preferred that the feed be a low-cost, coarser form of composition desired. However, if the coarse form is expensive, it is equally feasible to use a mix of low-cost precursors that when combined reflect the composition desired. While stoichiometry is preferred, non-stoichiometric feed ratios can be used if the non-stoichiometric feed is less expensive or if the final product streams have the properties as desired. The feed can be a pure composition, a mix of solids and reactant gases, a mix of solids and reactant liquids, a mix of solids, a mix of liquids and gases, a mix of liquids, a mix of gases, a mix of solids, liquids and gases, or combinations thereof. In one preferred embodiment, essentially the only constituent atoms present in the feed other than inert components are the constituent atoms

present in the desired solid product. There may be very minor impurity atoms in the feed, but undesired atoms are not present to any significant extent. As an example, if the desired oxide product is nanoscale zinc oxide (ZnO), the feed would be micron scale zinc oxide. If the desired product is indium tin oxide (ITO) the feed would be indium oxide and tin oxide. If the desired product is nonstoichiometric titanium dioxide, the feed would be titanium dioxide and the process would be run to produce a non-stoichiometric product. An example of a system which would not represent this embodiment would be the reaction of titanium tetrachloride with water to produce titanium dioxide and hydrogen chloride as follows:



In this case there are constituent atoms present in the feed, namely hydrogen and chlorine, which are not present in the desired solid product.

The preferred method is premixing the feed to as homogeneous levels as possible. However, heterogeneous, series, or parallel feeds are suitable for certain applications. The feed precursors are preferably carried in a gas or a mix of gases that does not possess or can contribute an element that is not desired in the final composition. A preferred carrier stream are inert gases such as argon, helium, neon and xenon. The powder 10 is then suspended in the gas 12, preferably in a continuous operation, using fluidized beds, spouting beds, hoppers, or combinations thereof, as best suited to the nature of the precursor. The test runs performed to reduce the invention to practice were conducted with precursor feeds having particle size greater than 1 micrometer, but the process could be used with any size suitable for its continuous vaporization in a gas stream. The resulting gas-stream suspension 16 is advantageously preheated in a heat exchanger 18 and then is fed into a thermal reactor 20 where the suspended powder particles preferably completely evaporated in a thermal evaporation zone 22 by the input of thermal energy. The dimensions of the hot zone are established based on energy balance equations derived from basic principles of transport phenomena. The temperature histories of the feed material depend upon the enthalpy of the plasma discharge and the thermodynamic properties of the feed material. The times required for heating the particulate material to the

melting point, melting, heating to the vaporization point and vaporization are calculated using heat transfer equations. Additionally, the steps of heating up to the melting temperature and boiling point, and melting and vaporization can be described using appropriate heat transfer equations. These equations can be found in the U.S. Provisional patent application Express Mail number EI813191155US dated August 26, 1997, and in Transport Phenomena in Metallurgy, G.H. Geiger and D. R. Pourier, Addison-Wesley Publishing Co., Reading, MA, USA (1973) both of which are included herein by reference. The source 24 of such thermal energy can be accomplished by external heat transfer or by internal heat or both. Examples of external heat include but are not limited to induction, d.c. arc, plasma and radiation. Examples of internal heat include, but are not limited to reaction heat such as combustion and latent heats of phase transformation. Any of these may be used so long as they are sufficient to cause the rapid vaporization of the powder suspension being processed. It is desirable that the temperature in the thermal evaporation zone be in excess of 2000 degrees C. It is preferred that the temperature in the thermal evaporation zone be in excess of 3000 degrees K. It is more preferred that the temperature in the thermal evaporation zone be in excess of 4000 degrees K. It is most preferred that the T in the thermal evaporation zone be in excess of 5000 degrees K. It is necessary that the temperature in the thermal evaporation zone be above the vaporization temperature of all constituent species. Optionally, in order to prevent contamination of the vapor stream caused by partial sublimation or vaporization of the thermal reactor's interior walls, they may be pre-coated with the same material being processed. Additionally, this problem can be prevented most preferably by actively cooling the reactor walls and by using a confinement gas stream, i.e. a blanket of the inert gases along the walls of the reactor.

The vaporized gas-stream suspension next enters an extended reaction zone 26 of the thermal reactor that provides additional residence time, as needed to complete the evaporation of the feed material and to provide additional reaction time (if necessary). It is desirable that the temperature in the extended reaction zone be in excess of 2000 degrees C. It is preferred that the temperature in the extended reaction zone be in excess of 2500 degrees K. It is more preferred that the temperature in the extended reaction zone be in excess of 3000 degrees K. It is necessary that the

temperature in the extended reaction zone be above the vaporization temperature of all constituent species. In some cases, this may mandate a temperature in excess of 3000 degrees K. As the stream leaves the reactor, it passes through a zone where the thermokinetic conditions favor the nucleation of solid powders from the vaporized precursor. These conditions are determined by calculating the supersaturation ratio and critical cluster size required to initiate nucleation. Rapid quenching leads to high supersaturation which gives rise to homogeneous nucleation. The unstable vapor phase system self-nucleates on atomic clusters of critical size. Below the critical size, the clusters are unstable for a given supersaturation, while above the cluster size the free energy of the cluster is negative. For an ideal vapor phase, the radius of the critical cluster size is given by the relation

$$r_n = 2\gamma V/kT \ln(P_i/P_\infty) \quad (2)$$

where γ is the surface free energy, V is the molecular volume of the condensed phase, k is Boltzman's constant, P_i is the pressure of the vapor in the system, and P_∞ is the vapor pressure of the condensed phase. See G. S. Springer, Advances in Heat Transfer, 14, 281-341, Academic Press (1978) which is included herein by reference.

Using titanium powder as an example, based on the physical properties of the feed material and operating conditions in the reactor (size = 10μ , melting point = $1,660^\circ\text{C}$, boiling point $3,287^\circ\text{C}$, heat of vaporization of titanium = 10.985 Btu/g , hot gas temperature = $4,000^\circ\text{C}$), it is possible to calculate the residence time required for vaporization (2.32 msec for heating to melting point, 0.265 msec for melting, 5.24 msec for vaporization; total time required = 8-10 msec). Based on the velocity of the suspension injected into the reactor and the travel distance through the reactor, one can determine that a velocity of about 46 ft/sec produces a residence time of 10.7 msec, sufficient for vaporization. If the process requires a predetermined thermokinetic state of the powder being processed which can be enhanced by the presence of a particular gas, a kinetic gas feed (such as argon, helium, nitrogen, oxygen, hydrogen, water vapor, methane, air, or combinations thereof) can also be mixed with the precursor vapor to reach the desired thermokinetic state. As soon as the vapor has begun nucleation, the process stream is quenched in a converging-

diverging nozzle-driven adiabatic expansion chamber 30 at rates at least exceeding 10^3 K/sec, preferably greater than 10^6 K/sec, or as high as possible. As further detailed below, a cooling medium 32 is utilized for the converging-diverging nozzle to prevent contamination of the product and damage to the expansion chamber 30.

5 Additionally, the use of a confinement blanket gas stream all along the periphery of the product stream also prevents the deposition of nanometer clusters to the walls of the reactor from thermophoresis. Rapid quenching ensures that the powder produced is homogeneous, its size is uniform and the mean powder size remains in submicron scale. The quenching of the product gas, however, can be accomplished in numerous
10 ways and combinations thereof. Some additional examples include, but are not limited to, addition of coolant gases or liquids, addition of materials which absorb heat, radiative cooling, conductive cooling, convective cooling, application of a cooled surface, impinging into liquid such as but not limited to water. The preferred method however, is gas expansion as is described in detail below.

15 The theoretical behavior of the Joule-Thompson adiabatic expansion process is described by the well-known equation:

$$T_2/T_1 = (P_2/P_1)^{(k-1)/k}, \quad (3)$$

20 where T_1 and T_2 are the temperatures before and after expansion, respectively; P_1 and P_2 are the pressures before and after expansion, respectively; and k is the ratio of specific heats at constant pressure and constant volume (C_p/C_v).

Applying Equation 2 to a temperature change occurring during adiabatic expansion,
25 ΔT ,

$$\Delta T/T_1 = (T_2 - T_1)/T_1 = (P_2/P_1)^{(k-1)/k} - 1; \quad (4)$$

or, for a steady state process,

30

$$dT/dt = T_1 d[(P_2/P_1)^{(k-1)/k}]/dt, \quad (5)$$

which suggests that Joule-Thompson expansion can quench high-temperature vapors at a steady-state quench rate that depends on the rate at which the pressure is reduced across a given adiabatic expansion-device. Thus, in a continuous, steady-state process, the quench rate can be changed by changing the rate of expansion, which provides a much-sought form of control over the nucleation process of nanopowders produced by vapor condensation. Since it is known that the size, size distribution and other properties of vapor condensation products depend on the speed at which the nucleating material is quenched, the adiabatic expansion approach of the present invention provides an invaluable tool, missing in all prior-art processes, for controlling the quality of the resulting nanopowders. In addition, because the process can be carried out stably in continuous fashion, it provides a suitable vehicle for large scale applications and commercial production of bulk nanomaterials.

Figure 2a is a sketch of a converging-diverging nozzle 50 to illustrate the relationship between critical parameters of the process and of the nozzle used to carry out the invention. It consists of an optimally-shaped combination of a convergent section 52, a throat section 54, and a divergent section 56. At steady state, the condensing fluid is restricted through a uniformly decreasing cross-section A_1 from an initial cross-section A_1 at pressure P_1 and temperature T_1 , it is passed through the cross-section A^* of the throat 54, and then it is expanded through a final cross-section A_2 at pressure P_2 and temperature T_2 . The process is carried out through a cross-section A that is first uniformly decreasing and then uniformly increasing through the device. In the converging section 52, the Mach number M for the nozzle is less than 1, while it is equal to 1 in the throat 54, and greater than 1 in the diverging section 56. (Mach number is defined as the ratio of the hydrodynamic flow velocity to the local speed of sound.) Therefore, the initial subsonic flow is accelerated in the converging section of the nozzle, and the flow expands supersonically in the divergent section of the nozzle. At any cross-section A , the Mach number is given by the local value of A/A^* , with $m=1$ at the throat. Provided the flow is accelerated to a uniform design Mach number, the extent of cooling, pressure, and density drop can be predicted by the following one-dimensional relationships:

$$T_2/T_1 = [1 + (k-1)M^2/2]^{-1} \quad (6)$$

$$P_2/P_1 = [1 + (k-1)M^2/2]^{k/(k-1)} \quad (7)$$

$$\rho_2/\rho_1 = [1 + (k-1)M^2/2]^{1/(k-1)} \quad (8)$$

5 where T_2 , P_2 and ρ_2 are the flow temperature, pressure and density of the condensing fluid after the divergent section, T_1 , P_1 and ρ_1 , are at the inlet section of the nozzle, M is the Mach number, and K is the ratio of heat capacities at constant pressure and constant volume (C_p/C_v). See J.D. Anderson, Modern Compressible Flow, McGraw-Hill, N.Y., N.Y., (1990) which is included herein by reference.

10 Based on these equations, it is clear that the dimensions of the nozzle are key to its performance as a quenching device. In particular, by the selection of diameter and length of the three critical sections (52, 54 and 56) and the convergent and divergent angles of the corresponding sections, it is possible to design a nozzle that will produce the necessary Mach number to yield the desired quenching rate. A simple drawing of
15 such a converging-diverging nozzle is also shown in Fig. 2b to illustrate the key design parameters of the device. They are the diameter D_c , the length L_c and the converging angle Θ_c , for the converging section; the diameter D_d , the length L_d and the diverging angle Θ_d for the diverging section; and the diameter D_t , and length L_t , for the throat. In the preferred embodiment of the invention, the dimensions used on
20 the basis of the previously stated equations were as follows: $D_c = 3.0$ in, $L_c = 4.125$ in, $\Theta_c = 17.965^\circ$, $D_d = 0.75$ in, $L_d = 1.261$ in, $\Theta_d = 9.648^\circ$, $D_t = 0.325$ in, and $L_t = 0.114$ in.

For example, using argon as the medium, with a pressure drop of 0.72 atmospheres across the nozzle, a temperature drop of $T_2/T_1 = 0.54$ can be expected
25 across the nozzle. It should be noted that in the preferred nozzle, as further detailed below, besides the cooling effect due to expansion, the temperature drop across the nozzle is also enhanced by heat transfer with a boundary-layer gas blanket in the nozzle and by water cooling of the nozzle itself.

Referring back to Figs. 3a, 3b and 3c, the particulars of the nozzle 50 of the
30 invention, as adapted to a process for rapidly quenching condensing vapors to produce nanopowders, are illustrated in sectional-elevational and top views. For durability and continuous operation, it is necessary to keep the nozzle wall cool to

avoid contamination of the quenched product with the material of construction of the nozzle or, in worst cases, even to avoid melt down and structural failure of the nozzle. Keeping the nozzle wall cool enhances the quenching effect of the nozzle, leading to yet higher quench rates (exceeding 10^6 K/sec). Accordingly, as shown in Figure 3a, the temperature of the nozzle is maintained low with a coolant stream 32, such as cooling water, circulating in a cooling jacket 29 surrounding the nozzle's interior wall 58 between inlet and outlet ports 60 and 62. The cooling medium is preferably circulated in countercurrent flow to optimize uniform cooling of the wall.

In addition, although lower nozzle-wall temperatures improve the contamination and failure problems, such lower temperatures can also lead to vapor condensation on the nozzle walls because of mechanisms such as thermophoresis. Vapor condensation can, in turn, lead to increasing restriction in the nozzle throat diameter, with subsequent closure of the throat and failure of the nozzle. We solved this additional problem by providing a gaseous boundary-layer stream 33 to form a blanket over the internal surface of the nozzle. As shown in Figure 3c, the blanket gases can be introduced into the nozzle's interior wall axially, radially or tangentially, through an inlet port 31, and can be inert, such as argon or helium when metals and alloys are being processed; or reactive, such as nitrogen, when nitrides are being synthesized; or oxygen or air, when oxides are being processed; methane and hydrocarbons, when carbides are being processed; halogens when halides are being synthesized; or combinations thereof, depending on the ultimate material being synthesized. Thus, reactive gases can participate in heat transfer with the nucleation process, or reactively on powder surface to selectively modify the composition of the surface (coated powders), or reactively to transform the bulk composition of the powder, or in combinations to achieve multiple functions. This secondary gas feed 33 can help engineer the product nucleation process and the resultant characteristics of the powder. Such nanosize powders will be passivated by precision controlled exposure to N_2 , O_2 , CH_4 or NH_3 .

Referring back to Figure 1, the quenched gas stream 34 is then filtered in appropriate separation equipment 36 to remove the submicron powder product 38 from the gas stream. The separation can be accomplished using various methods including, but not limited to, bag houses containing polymeric or inorganic filters,

electrostatic filtration, surface deposition on cold surfaces followed by scraping with a blade, centrifugal separation, in situ deposition in porous media, adsorption in liquids or solids. The preferred method for use in the present invention, however, is the use of bag houses. As well understood in the art, the filtration can be accomplished by single stage or multistage impingement filters, electrostatic filters, screen filters, fabric filters, cyclones, scrubbers, magnetic filters, or combinations thereof. The filtered nanopowder product 38 is then harvested from the filter 36 either in batch mode or continuously using screw conveyors or phase solid transport and the product stream is conveyed to powder processing or packaging unit operations (not shown in the drawings). The filtered gas stream 40 is compressed in a vacuum-pump/compressor unit 42 and cooled by preheating the gas-stream suspension 16 in heat exchanger 18. Thus, the enthalpy of compression can be utilized by the process as process heat through heat integration. Stream 40 is then treated in a gas cleaning unit 44 to remove impurities and any undesirable process product gases (such as CO, CO₂, H₂O, HCl, NH₃, etc). The gas treatment can be accomplished by single stage or multistage gas-gas separation unit operations such as absorption, adsorption, extraction, condensation, membrane separation, fractional diffusion, reactive separation, fractional separation, and combinations thereof. Finally, the treated gases 46 are recycled back to be reused with the feed gas stream 12. A small split stream 48 of the compressed treated gas 46 is purged to ensure steady state operation of the continuous thermal process.

Additionally, the invention was reduced to practice in a pilot plant illustrated schematically in Fig. 4. This thermal reactor, system consists of an upper, cylindrical, thermal evaporation chamber 22 made of quartz and cooled by circulating water (not shown). The gas-stream suspension 16 is formed by mixing the solid feed material 10 fed by a powder feeder 11 with an inert gas stream 12, such as argon. The suspension 16 is injected continuously from the top of the thermal evaporation chamber 22 through a water-cooled injection probe 23 and it is heated inductively by means of a DC plasma torch. Note that for the smaller scale process an ICP torch was used as the heat torch. However, one problem associated with the ICP torch is its low thermal efficiency. For scaled up processes, the use of a DC plasma torch is more advantageous because it enables better thermal efficiency, higher feed rates, no RF

radiation shielding is required, and it is easily positionable as compared to the ICP torch. In a DC plasma torch, plasma is produced by electrical discharge between two electrodes in the presence of a gas. The classifications of plasma torches are based on the position of electrodes, for example, non-transferred or transferred arc modes. In the non-transferred arc mode, both the anode and the cathode are located in the torch and the arc is established between these electrodes. In the transferred arc mode, one electrode is located outside the torch, which may be the workpiece or material to be heated. In the scaled-up nanosize metal powders production unit, a non-transferred arc DC thermal plasma torch will be used as the heat source. The reactor also comprises another, cylindrical, extended reaction zone 26 made of stainless steel, water cooled, positioned downstream of the thermal evaporation zone 22, and sufficiently large to give the feed stream the residence time required to complete the vaporization and reaction. The reaction zone 26 is lined with a zirconia refractory felt and a layer of silicon-carbide refractory material to reduce heat losses from the hot reaction zone. If necessary to prevent contamination of the reacting fluid by the reactor or refractory material, the reactor's interior walls (and refractory lining) may be further lined with the same material constituting the solid feed.

The adiabatic expansion chamber 30 consists of a converging-diverging nozzle, as illustrated in Fig. 3a, operated with a pressure drop (created by the vacuum pump 42 operated at 50 to 650 Torr) sufficient for quenching the high-temperature vapors produced by plasma induction upstream in the reactor. The theoretical behavior or the Joule Thompson adiabatic expansion process has already been described above. After rapid quenching leading to homogeneous nucleation and nanosized powders, the powders are passivated by precision controlled exposure to N_2 , O_2 , CH_4 or NH_3 . The separation system of the invention is realized by means of a collection chamber 35, attached to the outlet of the expansion chamber 30, where the very fine particles entrained in the gaseous stream are collected on a water-cooled metallic coil 37 (copper was used successfully for the test runs detailed below) and periodically extracted. It is anticipated that commercial-scale equipment would incorporate a screw or similar conveyor for the continuous removal of the nanopowder product from the collection chamber 35. The gas stream 40 out of the collection chamber is further passed through a filter 39 and trap 41 to thoroughly clean it prior to passage

through the vacuum pump 42. A monitor and fluid-control panel 43 is utilized to monitor process variables (temperatures, pressures, water and gas flow rates), record them, and control all water and gas streams to maintain steady-state operation. It is noted that for simplicity the gas stream 48 exhausted from the vacuum pump 42 was not recycled in the demonstration plant of Fig. 4, but a commercial application would preferably do so for energy and material conservation. Additionally, Figures 5a, 5b, 5c, and 5d show the preferred embodiment of the present invention for a scaled up process.

Additionally, towards one of the goals of the present invention to produce a cost effective process, a detailed engineering cost analysis of the thermal process was performed for nanosize passivated aluminum powder. The results of the analysis suggested that the future total product cost for nanosize aluminum powder will be about 47.00/lb, therefore the first estimate for future nanosize aluminum powder market price was assessed at about 82.00/lb.

The effectiveness of the invention was demonstrated by utilizing the system of Fig. 2 to produce nanosize powders of several different materials. In each case, the powders harvested were characterized for phases, size, morphology, and size distribution. X-ray diffraction (XRD) was used to determine the phases present in the samples using a Siemens D5000 diffractometer with Ni-filtered Cu K α radiation. The peak widths for average grain size analysis were determined by a least-square fit of a Cauchy function. The average size of the powder produced was estimated by Scherrer's method. Transmission electron microscopy (Hitachi TEM H-8100 equipped with a Kevex® EDX) was used for size, morphology, and size distribution. The particle size of the powders produced was in the manometer range. Scanning electron microscopy (SEM) was used for the coarser size feed powders.

Example 1

Zinc: Commercially available zinc powder (-325 mesh) was used as the precursor to produce nanosize zinc powder. Feed zinc powder was fed into the thermal reactor suspended in an argon stream (argon was used as the plasma gas; the total argon flow rate was 2.5 ft³/min). The reactor was inductively heated with 16 kW of RF plasma to

over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250-Torr, but useful results were obtained at different pressure drops, ranging from 100 to 550 Torr. After undergoing a pressure drop of 100 to 550 Torr through the converging-diverging nozzle, the powder produced was separated from the gas by means of a cooled copper-coil-based impact filter followed by a screen filter. Fig. 6 is the TEM micrograph (or nanograph) of the nanosize powder produced by the invention, showing it to be in the 5-25 nanometer range. The size distribution was narrow, with a mean size of approximately 15 nm and a standard deviation of about 7.5 nm. Variations in the operating variables (such as power input, gas pressure, gas flow rates, and nozzle throat size) affected the size of the powder produced. An XRD pattern of the product is shown in Fig. 7, which indicates that the only phase present was zinc. To avoid condensation at the wall, argon was introduced tangentially (radial or axial injections have also been proven to be effective) at the nozzle walls. The inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

Example 2

20

Iron-Titanium Intermetallic: 2-5 micron powders of iron and 1025 micron powders of titanium were mixed in 1:1 molar ratio and fed into the thermal reactor suspended in an argon stream (total gas flow rate, including plasma gas, was 2.75 ft³/min). The reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and above 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 550 Torr. After undergoing a pressure drop of 100 to 550 Torr through the converging-diverging nozzle, the powder produced was separated from the gas by means of a cooled copper-coil-based impact filter followed by a screen filter. Fig. 8 is the SEM micrograph of the feed powders used, showing that they were greater than 1

micrometer when fed. Fig. 9 is a TEM image of nanopowders produced by the invention, showing them to be in the 10-45 nanometer range. The size distribution was narrow, with a mean size of approximately 32 nm and a standard deviation of about 13.3 nm. Variations in the operating variables affected the size of the powder produced. The XRD pattern of the product is shown in Fig. 10, which indicates that the phases formed were titanium, iron and iron-titanium intermetallic (FeTi). The phases present illustrate that the invention can produce nanoscale powders of metals and intermetallics. To avoid condensation at the wall, argon was introduced tangentially (radial or axial injections have also been proven to be effective) at the nozzle walls. The inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

Example 3

Nickel-Aluminum Intermetallic: 1-4 micron powders of nickel and 10-30 micron powders of aluminum were mixed in 1:1 molar ratio and fed into the thermal reactor suspended in an argon stream (total feed, including plasma gas, at 2.75 ft³/min). The reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and above 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 550 Torr. The powder produced was separated from the gas by means of a cooled copper-coil-based impact filter followed by a screen filter. Fig. 11 is a TEM image of the nanopowder produced by the invention, showing it to be in the 10-30 nanometer range. The size distribution was narrow, with a mean size of approximately 16.4 nm and a standard deviation of about nm. Variations in the operating variables affected the size of the powder produced. The XRD pattern of the product is shown in Fig. 12, which indicates that the phase formed was NiAl. The phases present illustrate that the invention can produce nanoscale powders of metals and intermetallics. To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The

inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

Example 4

5

Tungsten Oxide: Commercially available tungsten oxide powder (-325 mesh size) was used as the precursor to produce nanosize WO_3 . The tungsten oxide powder was suspended in a mixture of argon and oxygen as the feed stream (flow rates were 2.25 ft^3/min for argon and 0.25 ft^3/min for oxygen). The reactor was inductively heated
10 with 18 kW of RF plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 550 Torr. After undergoing
15 a pressure drop of 100 to 550 Torr through the converging-diverging nozzle, the powder produced was separated from the gas by means of a cooled copper-coil-based impact filter followed by a screen filter. Fig. 13 is the TEM nanograph of the WO_3 powder produced by the invention, showing it to be in the 10-25-manometer range. The size distribution was narrow, with a mean size of about 16.1 nm and a standard
20 deviation of about 6.3 nm. Variations in the operating variables (such as power input, gas pressure, gas flow rates, and nozzle throat size) affected the size of the powder produced. An XRD pattern of the product is shown in Fig. 14, which indicates that the phase present was WO_3 . To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary
25 layer to act as a barrier for any condensation on the nozzle walls.

Example 5

Cerium Oxide: Commercially available cerium oxide powder (5-10 micron size) was
30 used as the precursor to produce nanosize CeO_2 . The cerium oxide powder was suspended in a mixture of argon and oxygen as the feed stream (at total rates of 2.25 ft^3/Min for argon and 0.25 ft^3/min for oxygen). The reactor was inductively heated

with 18 kW of RF plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 650 Torr. The powder produced was separated from the gas by means of a cooled copper-coil-based impact filter followed by a screen filter. Fig. 15 is the TEM nanograph of the CeO_2 powder produced by the invention, showing it to be in the 5-25 manometer range. The size distribution was narrow, with a mean size of about 18.6 nm and a standard deviation of about 5.8 nm. Variations in the operating variables affected the size of the powder produced. An XRD pattern of the product is shown in Fig. 16, which indicates that the phase present was CeO_2 . To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

15

Example 6

Silicon Carbide: Commercially available silicon carbide powder (-325 mesh-size) was used as the precursor to produce nanosize SiC. The powder was suspended in argon as the feed stream (total argon flow rate of 2.5 ft³/min). The reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 550 Torr. The powder produced was separated from the gas by means of a cooled copper coil based impact filter followed by a screen filter. Fig. 17 is the TEM nanograph of the SiC powder produced by the invention, showing it to be in the 10-40 manometer range. The size distribution was narrow, with a mean size of approximately 28 nm and a standard deviation of about 8.4 nm. Variations in the operating variables affected the size of the powder produced. An XRD pattern of the product is shown in Fig. 18, which indicates that the phase present was SiC. To avoid condensation at the wall, argon

was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

Example 7

5

Molybdenum Nitride: Commercially available molybdenum oxide (MoO_3) powder (325 mesh size) was used as the precursor to produce nanosize Mo_2N . Argon was used as the plasma gas at a feed rate of $2.5 \text{ ft}^3/\text{min}$. A mixture of ammonia and hydrogen was used as the reactant gases (NH_3 at $0.1 \text{ ft}^3/\text{min}$; H_2 at $0.1 \text{ ft}^3/\text{min}$). The reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 550 Torr. The powder produced was separated from the gas by means of a cooled copper coil based impact filter followed by a screen filter. Fig. 19 is the TEM nanograph of the Mo_2N powder produced by the invention, showing it to be in the 5-30 nanometer range. The size distribution was narrow, with a mean size of about 14 nm and a standard deviation of about 4.6 nm. Variations in the operating variables affected the size of the powder produced. An XRD pattern of the product is shown in Fig. 20, which indicates that the phase present was Mo_2N . To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

25

Example 8

Nickel Boride Ceramic: 10 50 micron powder of nickel boride were fed into the thermal reactor with argon (fed at a total rate, including plasma gas, of $2.75 \text{ ft}^3/\text{min}$). once again, the reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging diverging nozzle. The preferred pressure drop across the nozzle was

30

250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 550 Torr. The powder produced was separated from the gas by means of a cooled copper coil based impact filter followed by a screen filter. Fig. 21 shows the SEM micrograph of the feed powders used, demonstrating that they were greater than 1 micrometer when fed. Fig 22 is the TEM nanograph of the Ni_3B powder produced by the invention, showing it to be in the 10 to 30 nanometer range. The size distribution was narrow, with a mean size of about 12.8 nm and a standard deviation of about 4.2 nm. Variations in the operating variables affected the size of the powder produced. An XRD pattern of the product is shown in Fig. 23, which indicates that the phase present were Ni and Ni_3B . To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer to act as a barrier for any condensation on the nozzle walls.

Example 9

Oxide Ceramics: 5-10 micron powders of calcium carbonate were fed into the thermal reactor with argon (at 2.5 ft³/min). The reactor was inductively heated with 16 kW of RF plasma to over 5,000 K in the plasma zone and about 2,500 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched by thermal expansion to about 100 Torr. The pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 50 to 550 Torr. The powder produced was separated from the gas by means of a cooled copper coil based impact filter followed by a screen filter. Fig. 24 is the TEM image of powder produced by the invention, showing it to be in the 5 to 20 nanometer range. As expected from the calcination reaction occurring in the reactor, the XRD data (shown in Fig. 25) established that the main phase of the nanopowder was CaO. Some other phases, such as $\text{Ca}(\text{OH})_2$, were also present due to exposure to atmospheric moisture. The size distribution of the CaO was narrow, with a mean size of about 14.8 nm and standard deviation of about 3.8 nm.

An alternate run was made with MgCO_3 powders with mean size of about 7 microns processed with argon. Once again, nanoscale powders of MgO were

produced as evidenced by TEM and XRD data. The final product powder size was observed to vary with changes in the pressure, temperature, flow rate, and compositions.

Example 10

5 Barium titanate (BaTiO_3): Commercially available barium titanate, micron size (5-10 micron) was used as the precursor to produce nanosize barium titanate powder. The feeding was calibrated to this required feed rate by adjusting the power feeder and the flow rate of the carrier gas. The reactor was inductively heated with 18 kW of
10 RFplasma to a thermal steady state. Thermal steady state was established by monitoring the temperature in the reactor. Feed barium titanate powder was feed into the thermal reactor suspended in an argon stream at a gas flow rate of 1.0 ft.³/min. The power was turned off and the system allowed to cool down under inert conditions by keeping some flow of argon in the reactor. The product was collected from the
15 quench section and filter, weighed and saved for analysis and performance testing. TEM images of the powder produced are shown in Figures 26a and 26b. The X-ray diffraction pattern of the powder produced is shown in Figure 27.

An alternate run was made with strontium titanate (SrTiO_3) powder to produce
20 nanosize SrTiO_3 powder. The feed precursor for strontium titanate was micron size (5-10 microns) SrTiO_3 powder. TEM images of the produced powder are shown in Figures 28a and 28b. X-ray diffraction pattern of the powder produced is shown in Figure 29, which reveals that the main phase present is SrTiO_3 . The surface area of the powder produced was 22.3 m²/g. Most of the produced powder ranged from 10-
25 40 nm.

Additionally, another run was performed to produce nanosize barium titanate (BaTiO_3) powder by the following reaction



using commercially available barium carbonate (BaCO_3) and titanium oxide (TiO_2) powders. Both precursors had a size of -325 mesh and were obtained from a commercial supplier. As a result of this test using the abovementioned thermal reactor, nanosize powder of barium titanate was produced. TEM images of the powder produced are shown in Figures 30a and 30b. Figure 31 shows the X-ray diffraction pattern of the powder produced, which shows that the main phase present is BaTiO_3 . The surface area of the produced powder was $11.9 \text{ m}^2/\text{g}$. The powder produced was in the nanosize range (10-75 nm).

10

Example 11

Nickel Zinc Ferrite: Commercially available nickel zinc ferrite powder (-325 mesh) was used as a precursor to produce nanosize $\text{NiZnFe}_2\text{O}_4$ powder. Feed $\text{NiZnFe}_2\text{O}_4$ powder was fed into the thermal reactor suspended in an argon stream (argon and helium were used as the plasma gases; the total argon flow rate was $1.6 \text{ ft}^3/\text{min}$ and the helium flow rate was $0.57 \text{ ft}^3/\text{min}$). The reactor was heated with a 25 kW DC plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 650 Torr. The powder produced was separated from the gas by means of a cooled copper coil-based impact filter followed by a screen filter. Figure 32 is the TEM nanograph of the $\text{NiZnFe}_2\text{O}_4$ powder produced by the invention, showing it to be in the 5-50 nanometer range. Variations in the operating variables affected the size of the powder produced. An XRD pattern of the product is shown in Figure 33, which indicates that the main phase present was $\text{NiZnFe}_2\text{O}_4$. To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer for any condensation on the nozzle walls.

30

Example 12

Nickel-Chromium-Cobalt-Molybdenum Alloy: Commercially available nickel-chromium-cobalt-molybdenum alloy powder (-325 mesh) was used as a precursor to

produce nanosize Ni-Cr-Co-Mo powder. Feed Ni-Cr-Co-Mo powder was fed into the thermal reactor suspended in an argon stream (argon was used as the plasma gas; the total argon flow rate was 2.5 ft³/min). The reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 650 Torr. The powder produced was separated from the gas by means of a cooled copper-coil-based impact filter followed by a screen filter. Figure 34 is the TEM nanograph of the Ni-Cr-Co-Mo powder produced by the invention, showing it to be in the 5-100 nanometer range. Variations in the operating variables affected the size of the powder produced. An XRD pattern of the product is shown in Figure 35, which indicates that the main phase present was Ni-Cr-Co-Mo with minor amounts of NiCr₂O₄ and Ni₃TiO₅. To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer for any condensation on the nozzle walls.

Example 13

Bismuth Telluride: Commercially available bismuth telluride powder (-325 mesh) was used as a precursor to produce nanosize Bi₂Te₃ powder. Feed Bi₂Te₃ powder was fed into the thermal reactor suspended in an argon stream (argon was used as the plasma gas; the total argon flow rate was 2.5 ft³/min). The reactor was inductively heated with 18 kW of RF plasma to over 5,000 K in the plasma zone and about 3,000 K in the extended reactor zone adjacent the converging portion of the nozzle. The vaporized stream was quenched through the converging portion of the nozzle. The vaporized stream was quenched through the converging-diverging nozzle. The preferred pressure drop across the nozzle was 250 Torr, but useful results were obtained at different pressure drops, ranging from 100 to 650 Torr. The powder produced was separated from the gas by means of a cooled copper-coil-based impact filter followed by a screen filter. Figure 36 is the TEM nanograph of the Bi₂Te₃ powder produced by the invention, showing it to be in the 20-100 nanometer range. Variations in the operating variables affected the size of the powder produced. An

XRD pattern of the product is shown in Figure 37, which indicates that the phase present was Bi_2Te_3 . To avoid condensation at the wall, argon was introduced tangentially at the nozzle walls. The inert gas provided cooling as well as a boundary layer for any condensation on the nozzle walls.

5

These examples demonstrate the feasibility and effectiveness of the principles of this invention in producing nanosize powders from micron sized precursors. The process and apparatus of the invention, utilizing ultra rapid quenching as the process step for the formation of nanopowders, provide a practical method for controlling the size of the product by manipulating process parameters. In particular, by controlling the quenching rate by changing the pressure drop over the expansion nozzle of the invention, we found that predetermined particle sizes and size distributions can be produced reliably in a continuous, steady state process, which is easily scaleable for commercial bulk production. The process was proven viable for metals, alloys, intermetallics, ceramics, composites, and combinations thereof. In addition, we demonstrated that the process can utilize feeds of reactive components and produce submicron powders of corresponding thermodynamically stable or metastable product species at high temperatures; that it is suitable for recycling and reusing product gases as feed gases; and for recycling and reusing any unseparated product powders as feed material. The method and apparatus of the invention solve many problems unresolved by existing processes to produce submicron powders in general and nanostructured materials in particular. Especially, the process is scaleable; it is solvent free and therefore inherently non polluting and of low cost; it is flexible in relation to processing different feed materials; it allows simple control of product powder size and size distribution; and it does not utilize contaminating components in the feed or for processing, therefore yielding product powders that are as pure as the powders fed to the process.

Inasmuch as one of the primary inventive concepts of the invention is the effective thermal quenching and the attendant advantages produced by ultra rapid expansion of a vaporized suspension of the feed material, it is clear that the concept could be applied as well to a system where the precursor material is in the form of a mass evaporated by any method in a low pressure gas. Similarly, the process is

30

applicable to liquid or gaseous precursors that are combined with one or more reactive gases in a reactor and then quenched ultra rapidly according to the invention to produce nanosize particles with a narrow size distribution. For example, silicon tetrachloride (normally liquid at room temperature) can be reacted with methane to produce a silicon carbide vapor which, rapidly quenched according to the invention, can produce a nanosize SiC powder. Similarly, silane (SiH_4 , normally gaseous at room temperature) can be reacted with methane to produce a silicon carbide vapor which can also be rapidly quenched to produce a nanosize SiC powder with a narrow size distribution. Finally, it is understood that specific changes in materials and procedures may be made by one skilled in the art to produce equivalent results.

Therefore, while the present invention has been shown and described herein in what is believed to be the most practical and preferred embodiments, it is recognized that departures can be made therefrom within the scope of the invention, which is therefore not to be limited to the details disclosed herein but is to be accorded the full scope of the claims so as to embrace any and all equivalent apparatus and methods.

1 What we claim is:

2

3 1. A process for producing a nanoscale powder from a precursor material

4 comprising the following steps:

5 evaporating the precursor material in a gaseous atmosphere in a thermal reactor,

6 thereby creating a vapor/gas mixture; and

7 quenching said vapor/gas mixture by effecting its expansion through a

8 predetermined pressure drop, thereby causing the formation of nanoscale particles of

9 product material in a product gas.

10

11 2. The process of claim 1, wherein said pressure drop in the quenching step is

12 sufficient to cause a temperature of the vapor/gas mixture to change at a rate of at

13 least 1,000 °C per second.

14

15 3. The process of claim 1, wherein said pressure drop in the quenching step is

16 sufficient to cause a temperature of the vapor/gas mixture to change at a rate of at

17 least 1,000,000 °C per second.

18

19 4. The process of claim 1, wherein the temperature of said thermal reactor is in

20 excess of 2000 degrees C.

21

22 5. The process of claim 1, wherein the temperature of said thermal reactor is in

23 excess of 5000 degrees K.

24

25 6. The process of claim 1, wherein the constituent atoms of said precursor material

26 consist essentially of the constituent atoms of said product material.

27

28 7. The process of claim 1, wherein said expansion through a predetermined

29 pressure drop is carried out by passing the vapor/gas mixture through a converging

30 diverging expansion nozzle.

31

- 1 8. The process of claim 7, wherein the temperature of said thermal reactor is in
2 excess of 2000 degrees C.
3
- 4 9. The process of claim 7, wherein the temperature of said thermal reactor is in
5 excess of 5000 degrees K.
6
- 7 10. The process of claim 7, wherein the constituent atoms of said precursor material
8 consist essentially of the constituent atoms of said product material.
9
- 10 11. The process of claim 7, wherein said pressure drop through the converging
11 diverging expansion nozzle is sufficient to cause a temperature of the vapor/gas
12 mixture to change at a rate of at least 1,000 °C per second.
13
- 14 12. The process of claim 7, wherein said pressure drop through the converging
15 diverging expansion nozzle is sufficient to cause a temperature of the vapor/gas
16 mixture to change at a rate of at least 1,000,000 °C per second.
17
- 18 13. The process of claim 7, wherein said pressure drop is between 50 and 650 Torr.
19
- 20 14. The process of claim 1, wherein said evaporation and quenching steps are
21 carried out on a continuous basis.
22
- 23 15. The process of claim 14, wherein said evaporation step is carried out by feeding
24 said precursor material to the thermal reactor as a suspension in said gaseous
25 atmosphere and by subjecting the suspension to an input of thermal energy.
26
- 27 16. The process of claim 15, wherein said thermal energy is at least partially
28 produced by an inductive source.
29
- 30 17. The process of claim 15, wherein said thermal energy is at least partially
31 produced by a microwave source.
32

- 1 18. The process of claim 15, wherein said thermal energy is at least partially
2 produced by an electric arc.
3
- 4 19. The process of claim 15, wherein said thermal energy is at least partially
5 produced by heat of reaction.
6
- 7 20. The process of claim 7, further comprising the step of providing a gaseous
8 boundary layer stream to form a blanket over an internal surface of the nozzle.
9
- 10 21. The process of claim 1, further comprising the step of coating an internal
11 surface of said thermal reactor with a layer of said precursor material.
12
- 13 22. The process of claim 21, wherein said expansion through a predetermined
14 pressure drop is carried out by passing the vapor/gas mixture through a converging
15 diverging expansion nozzle.
16
- 17 23. The process of claim 22, wherein said pressure drop through the converging
18 diverging expansion nozzle is sufficient to cause a temperature of the vapor/gas
19 mixture to change at a rate of at least 1,000 °C per second.
20
- 21 24. The process of claim 21, further comprising the step of providing a gaseous
22 boundary layer stream to form a blanket over an internal surface of the nozzle.
23
- 24 25. The process of claim 1, further comprising the step of separating said
25 nanoscale particles of product material from said product gas.
26
- 27 26. The process of claim 25, further comprising the step of recycling said product
28 gas by feeding the product gas to the thermal reactor with said precursor material.
29
- 30 27. The process of claim 7, wherein said nanoscale powder is free of any
31 byproducts.
32

- 1 28. The process of claim 7, wherein said process is a physical process.
2
- 3 29. A nanoscale powder having a mean size less than 100 nm and a size
4 distribution with a standard deviation less than 25 nm produced by the process of
5 claim 1.
6
- 7 30. A nanoscale powder having a mean size less than 100 nm and a size
8 distribution with a standard deviation less than 25 nm produced by the process of
9 claim 13.
10
- 11 31. A nanoscale powder having a mean size less than 100 nm and a size
12 distribution with a standard deviation less than 25 nm produced by the process of
13 claim 14.
14
- 15 32. A nanoscale powder having a mean size less than 100 nm and a size
16 distribution with a standard deviation less than 25 nm produced by the process of
17 claim 20.
18
- 19 33. A nanoscale powder having a mean size less than 100 nm and a size
20 distribution with a standard deviation less than 25 nm produced by the process of
21 claim 21.
22
- 23 34. A nanoscale metal alloy powder having a mean size less than 100 nm and a
24 size distribution with a standard deviation less than 25 nm produced by the process of
25 claim 1.
26
- 27 35. A nanoscale metal oxide powder having a mean size less than 100 nm and a
28 size distribution with a standard deviation less than 25 nm produced by the process of
29 claim 1.
30

1 36. A nanoscale carbide powder having a mean size less than 100 nm and a size
2 distribution with a standard deviation less than 25 nm produced by the process of
3 claim 1.

4

5 37. A nanoscale nitride powder having a mean size less than 100 nm and a size
6 distribution with a standard deviation less than 25 nm produced by the process of
7 claim 1.

8

9 38. A nanoscale ceramic powder having a mean size less than 100 nm and a size
10 distribution with a standard deviation less than 25 nm produced by the process of
11 claim 1.

12

13 39. A complex nanoscale powder having a mean size less than 100 nm and a size
14 distribution with a standard deviation less than 25 nm produced by the process of
15 claim 1.

16

17 40. A complex nanoscale powder having a mean size less than 100 nm and a size
18 distribution with a standard deviation less than 25 nm produced by the process of
19 claim 7.

20

21 41. A complex nanoscale powder having a mean size less than 100 nm and a size
22 distribution with a standard deviation less than 25 nm produced by the process of
23 claim 13.

24

25 42. A complex nanoscale powder having a mean size less than 100 nm and a size
26 distribution with a standard deviation less than 25 nm produced by the process of
27 claim 14.

28

29 43. A complex nanoscale powder having a mean size less than 100 nm and a size
30 distribution with a standard deviation less than 25 nm produced by the process of
31 claim 20.

32

1 44. A complex nanoscale powder having a mean size less than 100 nm and a size
2 distribution with a standard deviation less than 25 nm produced by the process of
3 claim 21.

4
5 45. Apparatus for producing a nanoscale powder from a precursor material
6 comprising, in combination: means for evaporating said precursor material in a
7 gaseous atmosphere at a predetermined minimum evaporation temperature, thereby
8 creating a vapor/gas mixture; and means for quenching said vapor/gas mixture by
9 effecting its expansion through a predetermined pressure drop, thereby causing the
10 formation of nanoscale particles of a product material.

11
12 46. The apparatus of claim 45, wherein the minimum evaporation temperature is
13 greater than 2000 degrees C.

14
15 47. The apparatus of claim 45, further comprising means for providing a gaseous
16 boundary layer stream to form a blanket over an internal surface of said means for
17 quenching the vapor/gas mixture by allowing its expansion through a predetermined
18 pressure drop.

19
20 48. The apparatus of claim 47, further comprising means for coating with a layer
21 of said precursor material an internal surface of said means for evaporating the
22 precursor material in a gaseous atmosphere.

23
24 49. A device for quenching a vapor stream of a precursor material to produce its
25 condensation into a nanoscale powder, comprising:
26 convergent means for channeling said vapor stream into a flow restriction of a
27 predetermined cross-section from an inlet zone of predetermined inlet pressure;
28 divergent means for channeling said vapor stream out of said flow restriction
29 to an outlet zone of predetermined outlet pressure; and
30 means for maintaining said inlet and outlet pressures, thereby creating a
31 pressure differential therebetween;

1 wherein said pressure differential and said cross-section of the flow restriction
2 are selected to produce a quenching of said vapor stream at a rate of at least 1,000 K
3 per second.
4

5 50. The device of claim 49, further comprising means for cooling an internal
6 surface thereof.
7

8 51. The device of claim 49, further comprising means for providing a gaseous
9 boundary-layer stream to form a gas blanket over an internal surface of the device.
10

11 52. The device of claim 49, further comprising means for cooling an internal
12 surface thereof, and means for providing a gaseous boundary-layer stream to form a
13 gas blanket over an internal surface of the device.
14

15 53. The device of claim 49, wherein said convergent means, flow restriction and
16 divergent means consist of a convergent-divergent nozzle having uniformly
17 converging and diverging sections.
18

19 54. The device of claim 53, further comprising means for cooling an internal
20 surface of the device.
21

22 55. The device of claim 53, further comprising means for introducing a reactive
23 gas into the device.
24

25 56. The device of claim 53, further comprising means for providing a gaseous
26 boundary-layer stream to form a gas blanket over an internal surface of the device.
27

28 57. The device of claim 53, further comprising means for cooling an internal
29 surface of the device, and means for providing a gaseous boundary-layer stream to
30 form a gas blanket over an internal surface of the device.
31

1 58. The apparatus of claim 45, in which said product material consists essentially
2 of nanoscale particles of said precursor material.

3
4 59. The apparatus of claim 58, wherein the minimum evaporation temperature is
5 greater than 2000 degrees C.

6
7 60. The apparatus of claim 58, further comprising means for cooling an internal
8 surface of said quenching means.

9
10 61. The apparatus of claim 58, further comprising means for providing a gaseous
11 boundary-layer stream to form a gas blanket over an internal surface of said
12 quenching means.

13
14 62. The apparatus of claim 58, further comprising means for cooling an internal
15 surface of said quenching means, and means for providing a gaseous boundary-layer
16 stream to form a gas blanket over an internal surface of said quenching means.

17
18 63. The apparatus of claim 58, further comprising means for coating with a layer
19 of said precursor material an internal surface of said means for evaporating the
20 precursor material in a gaseous atmosphere.

21
22 64. The apparatus of claim 58, further comprising means for cooling an internal
23 surface of said quenching means; means for providing a gaseous boundary-layer
24 stream to form a gas blanket over an internal surface of said quenching means; and
25 means for coating with a layer of said precursor material an internal surface of said
26 means for evaporating the precursor material in a gaseous atmosphere.

27
28 65. The apparatus claim 58, wherein said quenching means consists of a
29 convergent-divergent nozzle having uniformly converging and diverging sections.

30
31 66. The apparatus of claim 64, further comprising means for cooling an internal
32 surface of said convergent-divergent nozzle.

1 67. The apparatus of claim 64, further comprising means for providing a gaseous
2 boundary-layer stream to form a gas blanket over an internal surface of said
3 quenching means.
4

5 68. The apparatus of claim 64, further comprising means for cooling an internal
6 surface of said convergent-divergent nozzle, and means for providing a gaseous
7 boundary-layer stream to form a gas blanket over an internal surface of said nozzle.
8

9 69. The apparatus of claim 64, further comprising means for coating with a layer
10 of said precursor material an internal surface of said means for evaporating the
11 precursor material in a gaseous atmosphere at a predetermined reactor pressure.
12

13 70. The apparatus of claim 64, further comprising means for cooling an internal
14 surface of said convergent-divergent nozzle; means for providing a gaseous
15 boundary-layer stream to form a gas blanket over an internal surface of said nozzle;
16 and means for coating with a layer of said precursor material an internal surface of
17 said means for evaporating the precursor material in a gaseous atmosphere.
18

19 71. A method of quenching a high-temperature vapor of a precursor material to
20 produce a nanoscale powder thereof, comprising the following steps:

21 (a) producing a vapor stream of said high-temperature vapor from an inlet
22 zone of predetermined inlet pressure and passing said vapor stream through a
23 convergent means to channel the vapor stream into a flow restriction of a
24 predetermined cross-section;

25 (b) channeling the vapor stream out of said flow restriction through
26 divergent means to an outlet zone of predetermined outlet pressure smaller than said
27 inlet pressure; and

28 (c) maintaining said inlet and outlet pressures, thereby creating a pressure
29 differential therebetween;

30 wherein said pressure differential and said cross-section of the flow restriction are
31 adapted to produce a supersonic flow of said vapor stream.
32

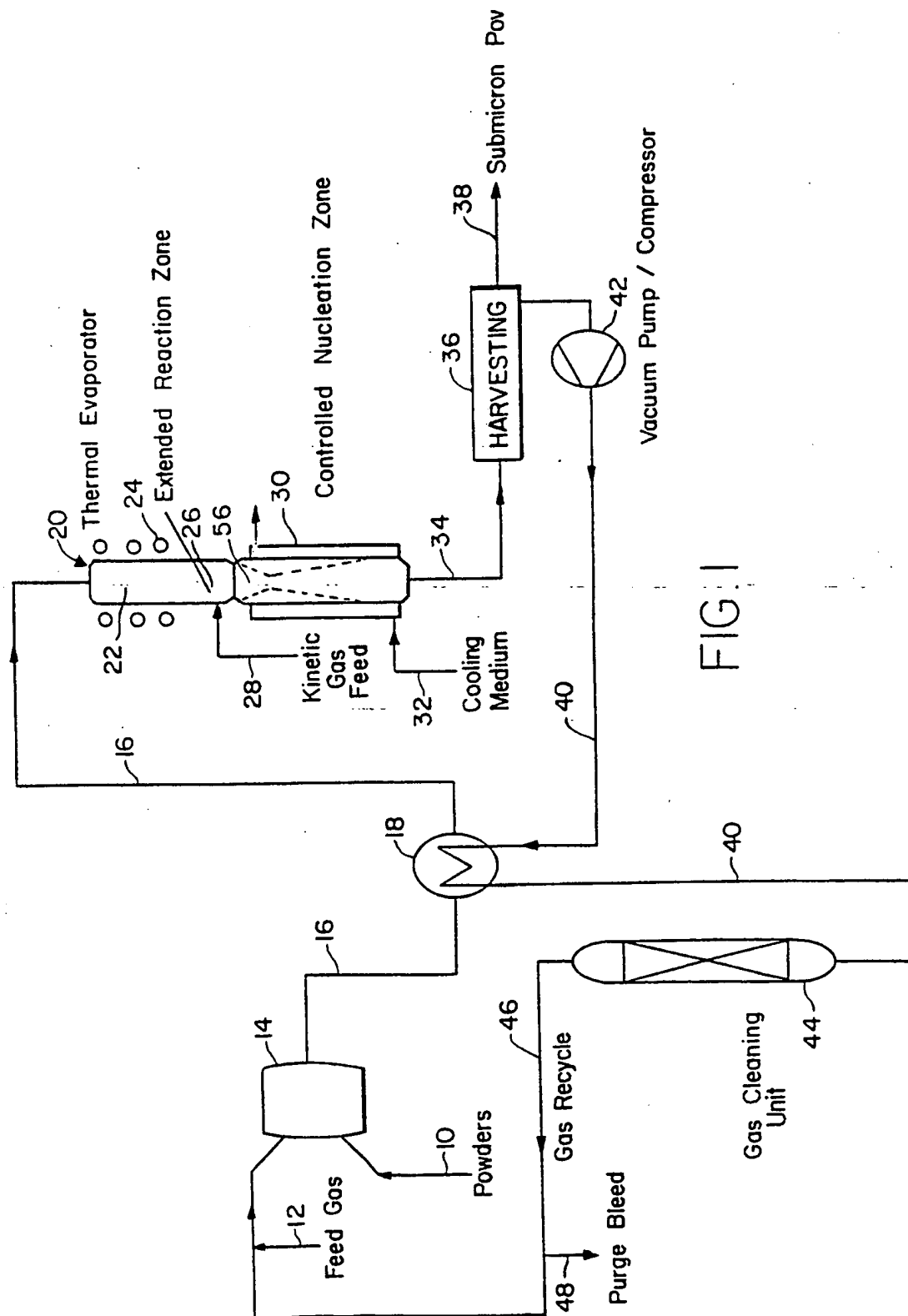
1 72. The method of claim 71, wherein said pressure drop in the quenching step is
2 sufficient to cause a temperature of the vapor/gas mixture to change at a rate of at
3 least 1,000 °C per second.

4

5 73. The method of claim 71, further comprising the step of providing a gaseous
6 boundary-layer stream to form a blanket over an internal surface of the convergent
7 means.

8

9



SUBSTITUTE SHEET (RULE 26)

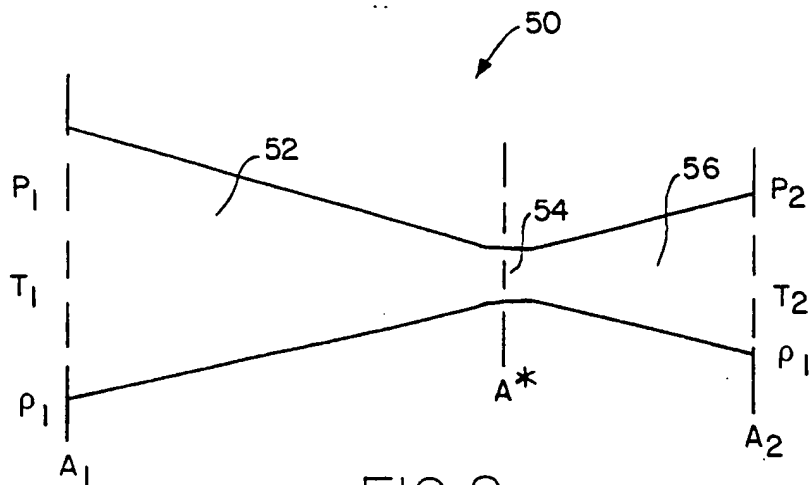


FIG. 2a

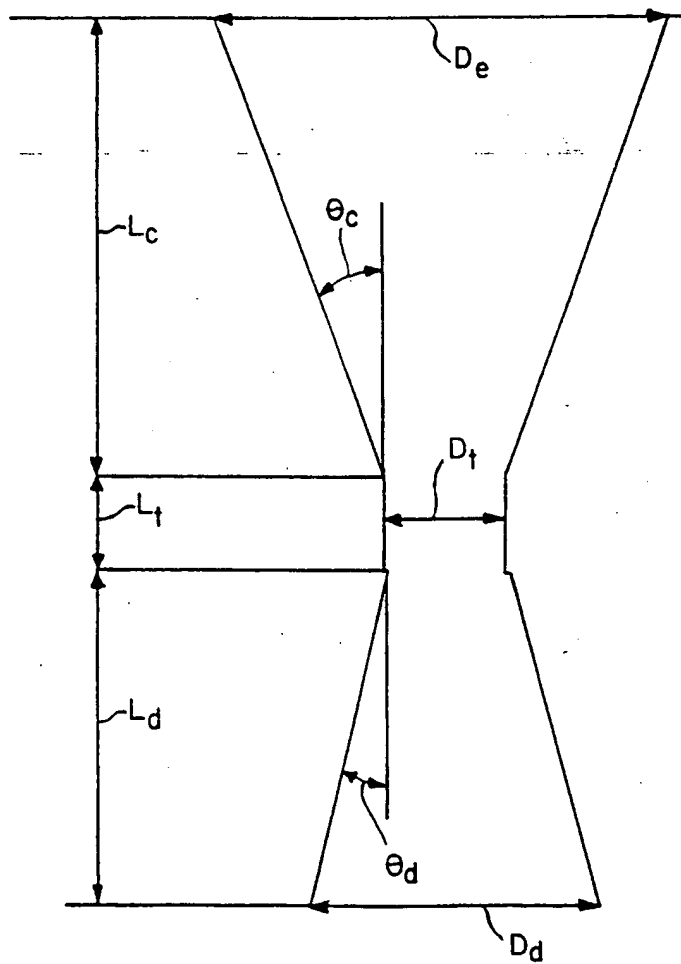


FIG. 2b

SUBSTITUTE SHEET (RULE 26)

3 / 28

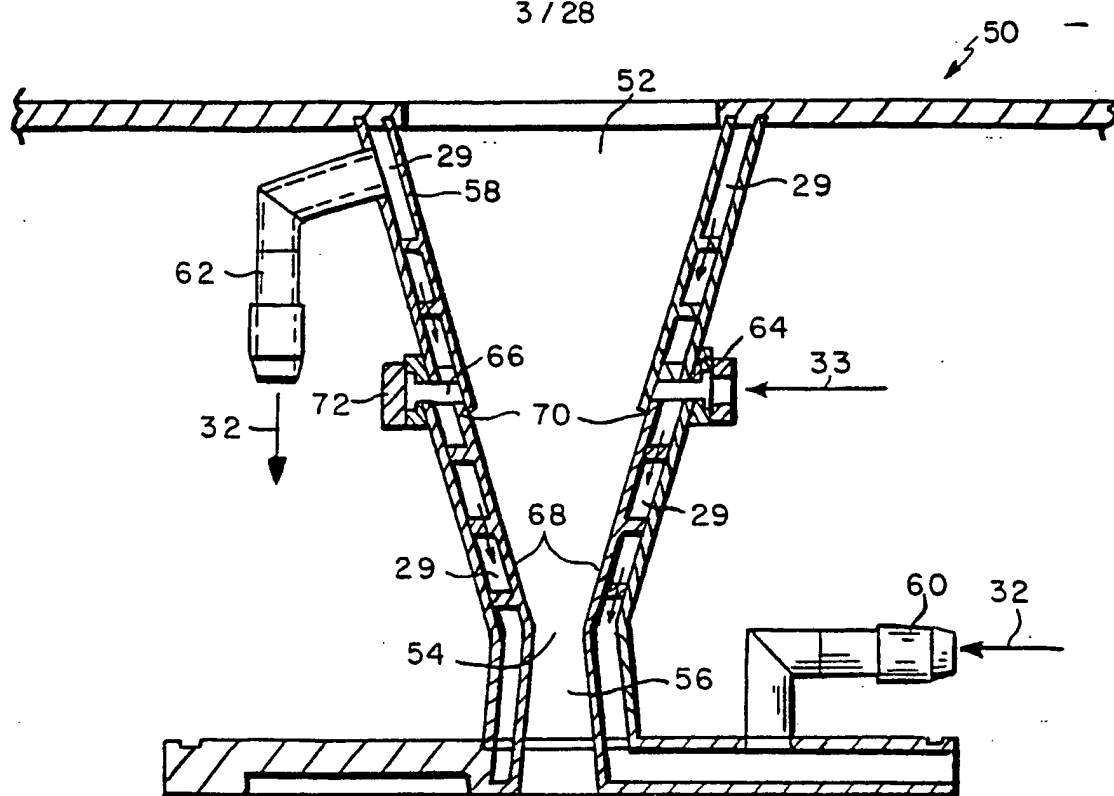


FIG. 3a

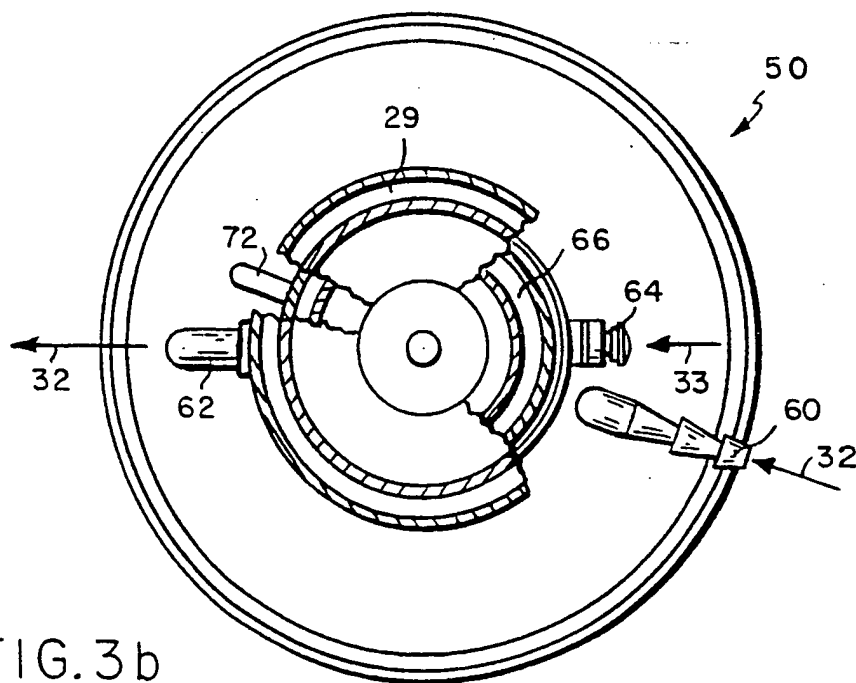


FIG. 3b

SUBSTITUTE SHEET (RULE 26)

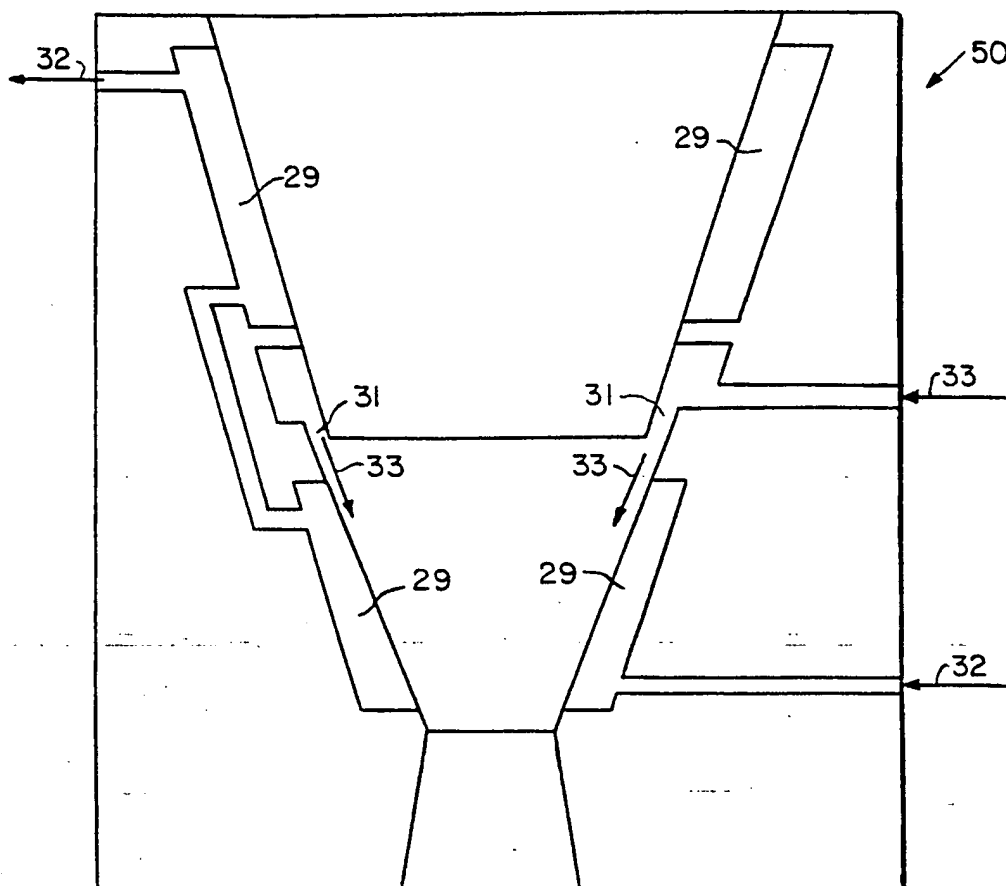
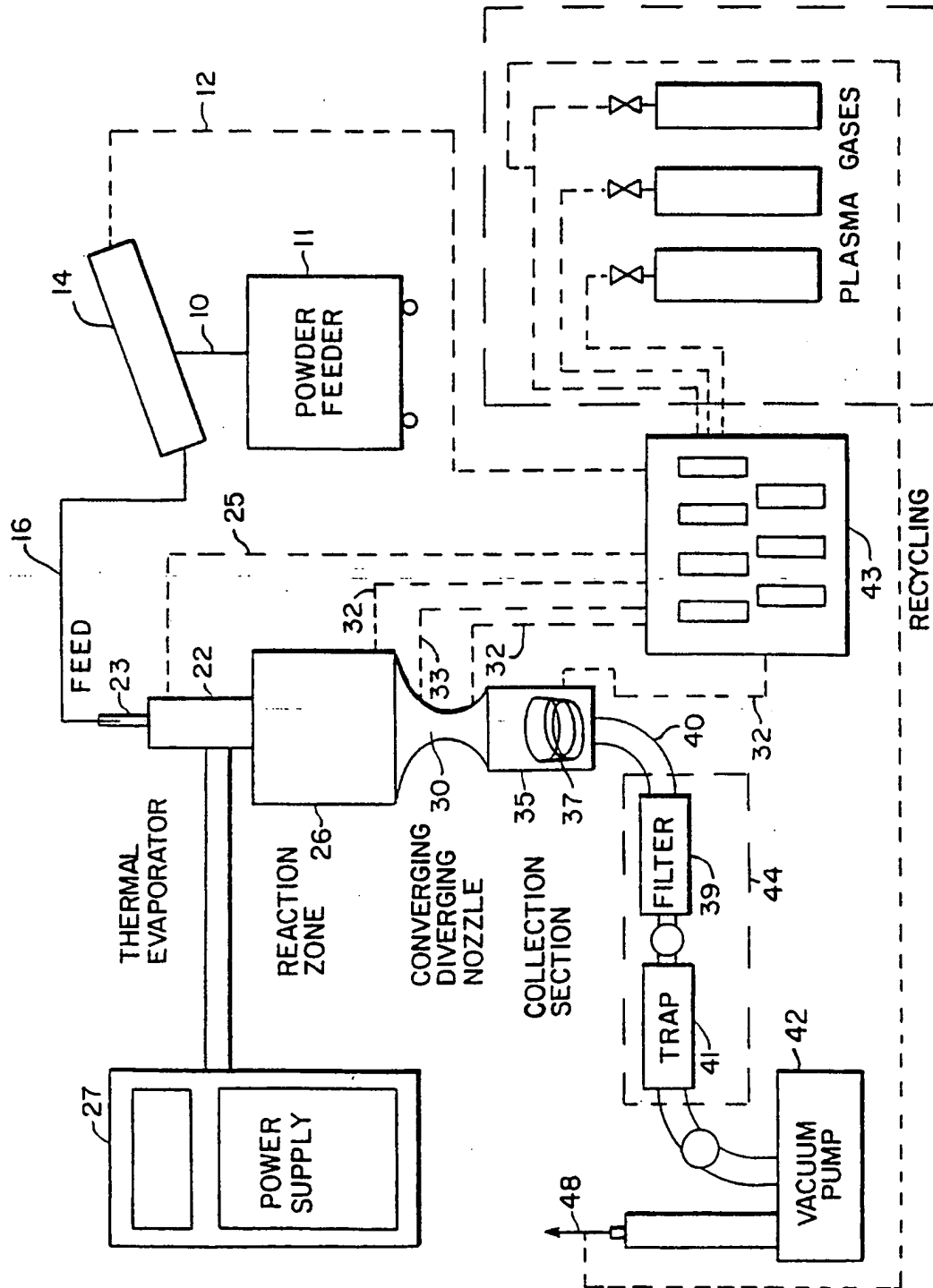


FIG. 3c

5/28

FIG. 4



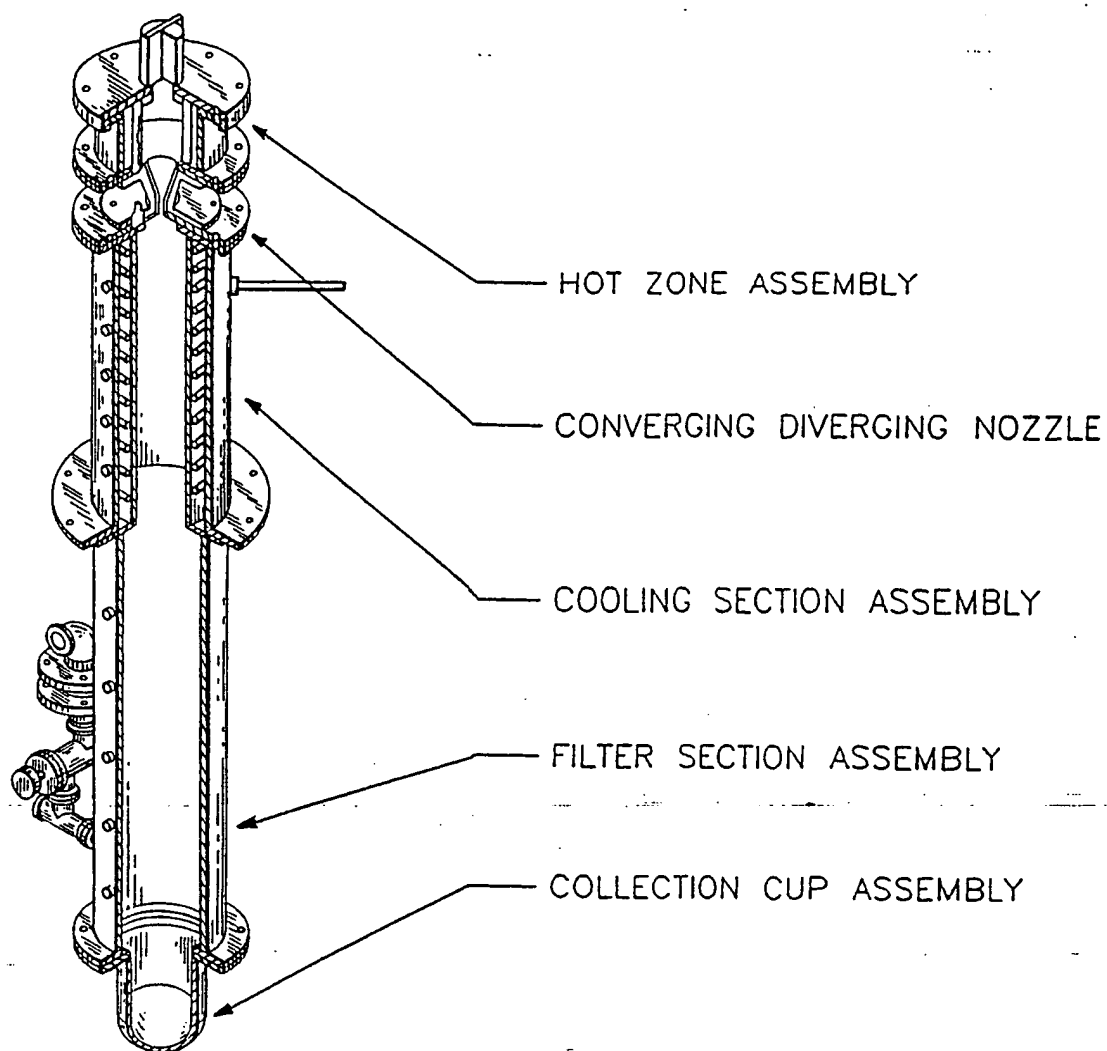


FIG. 5a

7/28

- 1 - DC Plasma Torch (100 KW) w / optional gas shroud [Nitrogen, Methane, Argon, Helium].
- 2 - Hot Zone - water cooled assembly. Incorporates Silicon carbide or graphite refractory, graphite felt and alumina insulation and electrically insulating nylon rings. Input ports for Thermocouple, pressure gauge, and reactive gases [Nitrogen, Methane, Oxygen, Ammonia].
- 3 - Converging / diverging valve, water cooled brass [Optional].
- 4 - Water cooled gas injection ring [Nitrogen, Methane, Oxygen, Ammonia].
- 5 - Cooling Section incorporated porous sintered Stainless Steel Tube wrapped with copper cooling tube. Side ports used for Thermocouples, pressure gauges, and process gases [Nitrogen, Oxygen, Argon, air].
- 6 - Passivation gas plate [Oxygen, Methane, Nitrogen, air].
- 7 - Filter Section collects powders on internal surface. Gas pressure pulsing on filter "knocks" powder loose. Five side ports used for pulsing gas, Thermocouples, and pressure gauges.
- 8 - Glass collection cup for powder retrieval.
- 9 - Burst Flange assembly ensures release of pressure in case of positive pressure buildup in side of reactor.
- 10 - Vacuum exhaust port to post filters and vacuum.

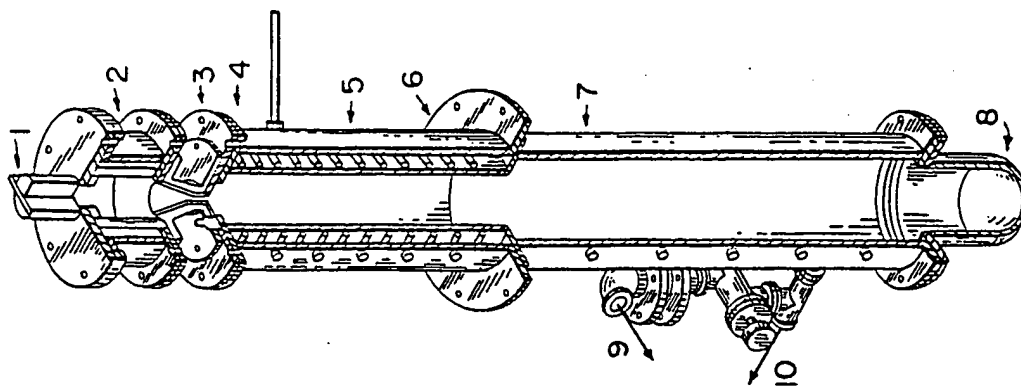


FIG. 5b

SUBSTITUTE SHEET (RULE 26)

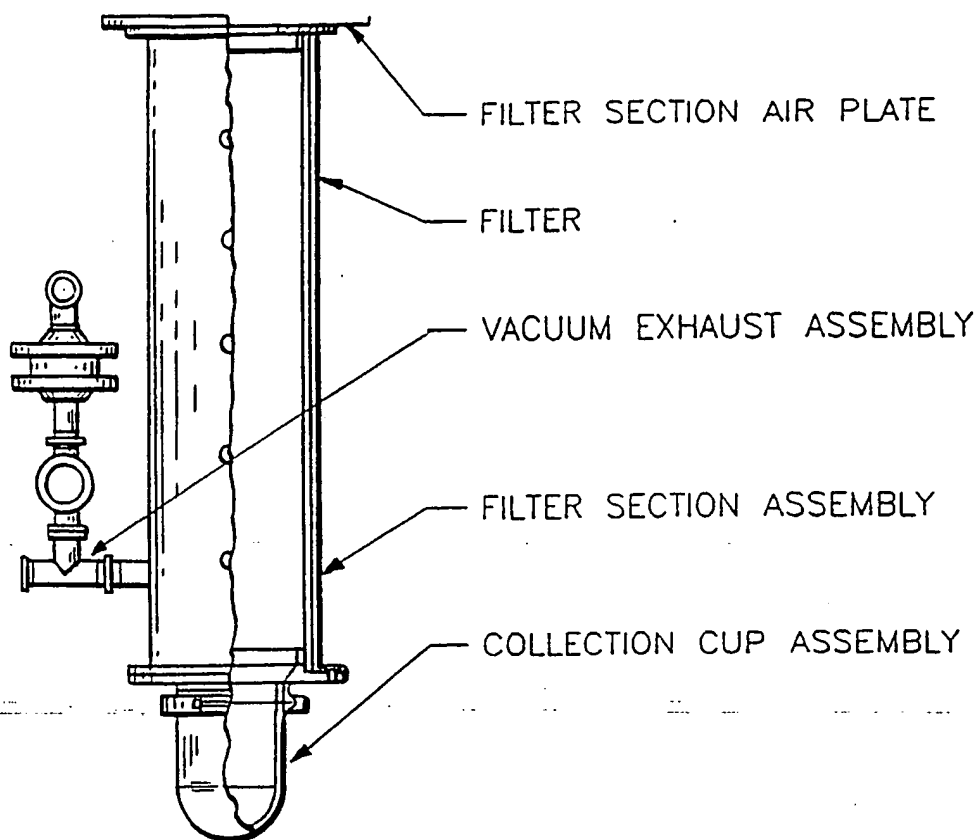


FIG. 5c

9 / 28

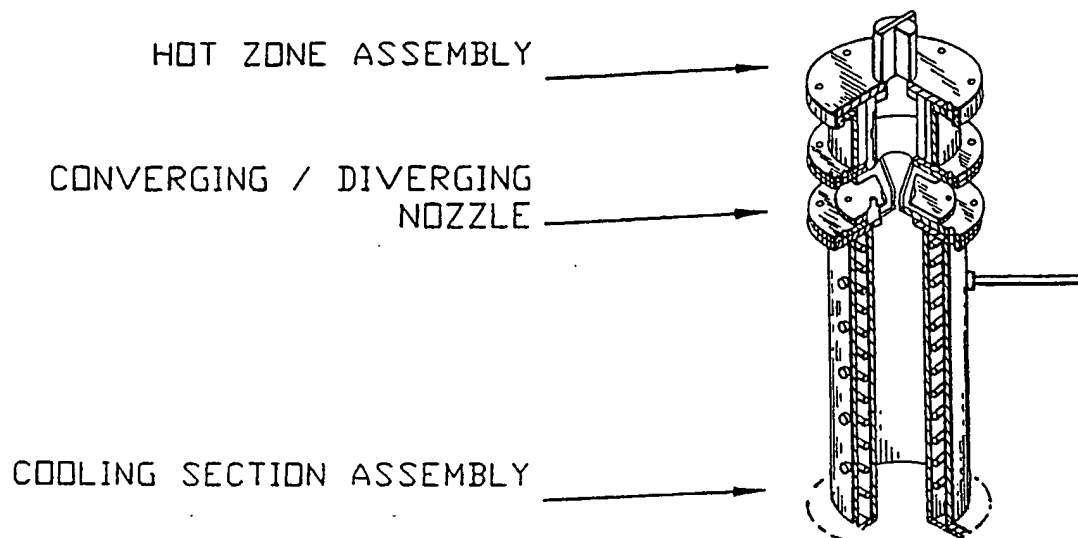


FIG. 5d

10/28

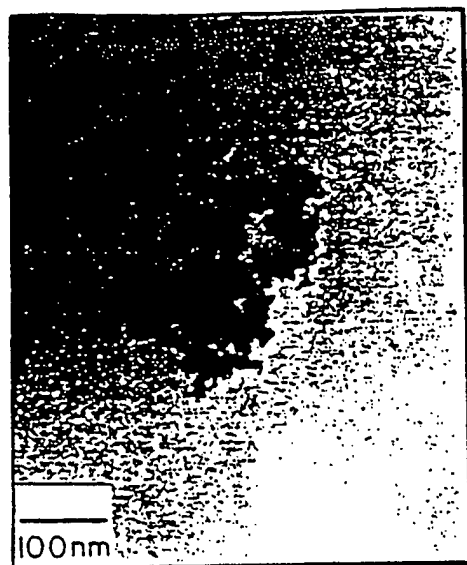


FIG. 6

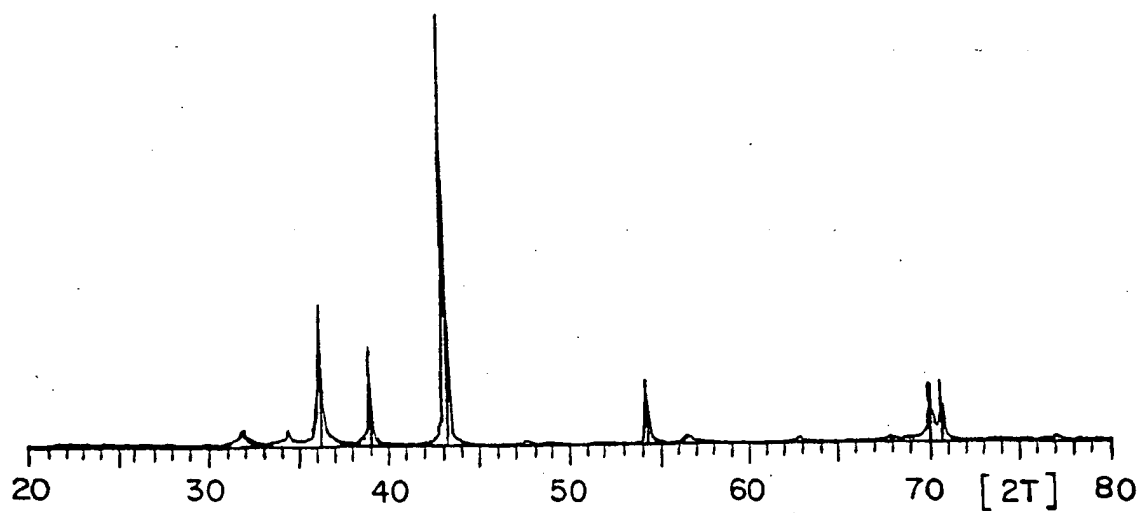


FIG. 7

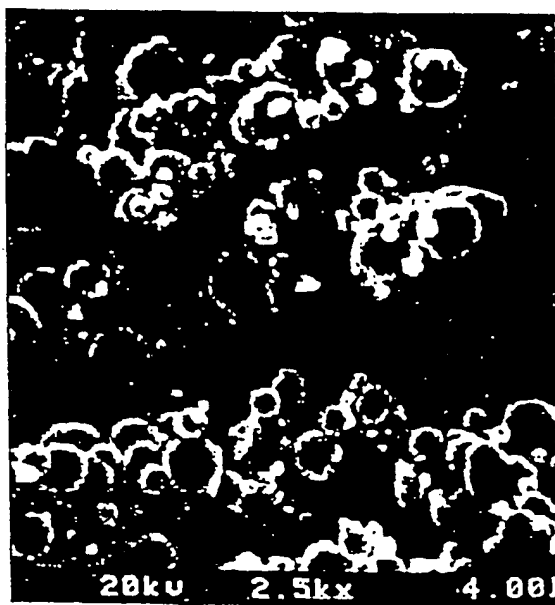
SUBSTITUTE SHEET (RULE 26)

11/28



Titanium

FIG. 8



Iron

12/28

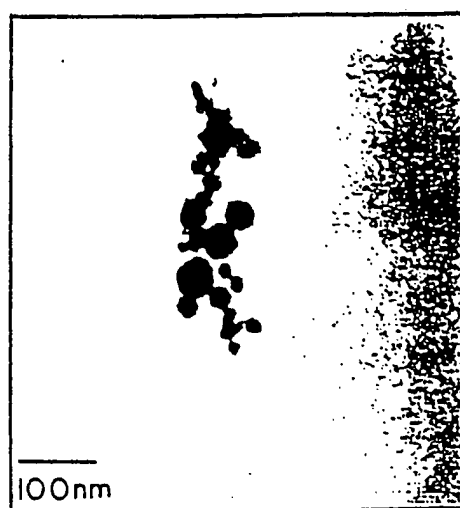


FIG. 9

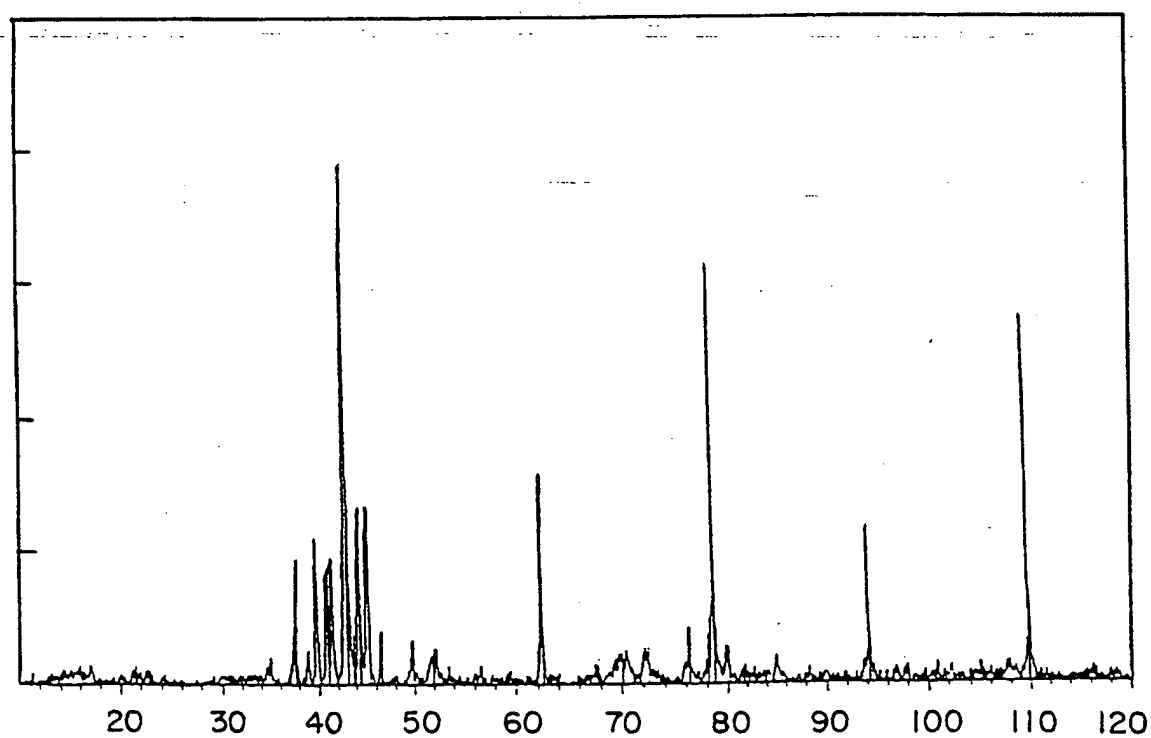


FIG. 10

SUBSTITUTE SHEET (RULE 26)

13/28

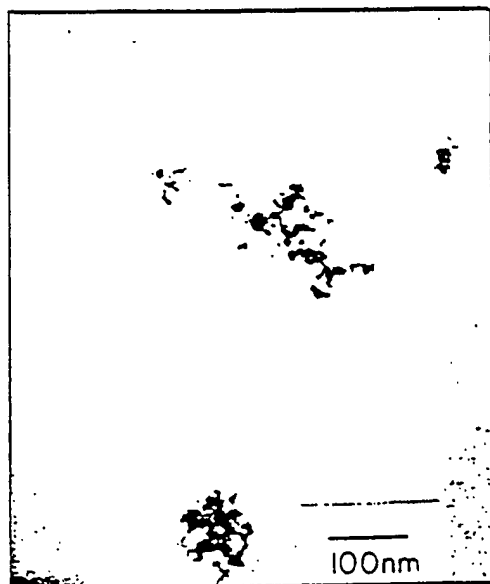


FIG. 11

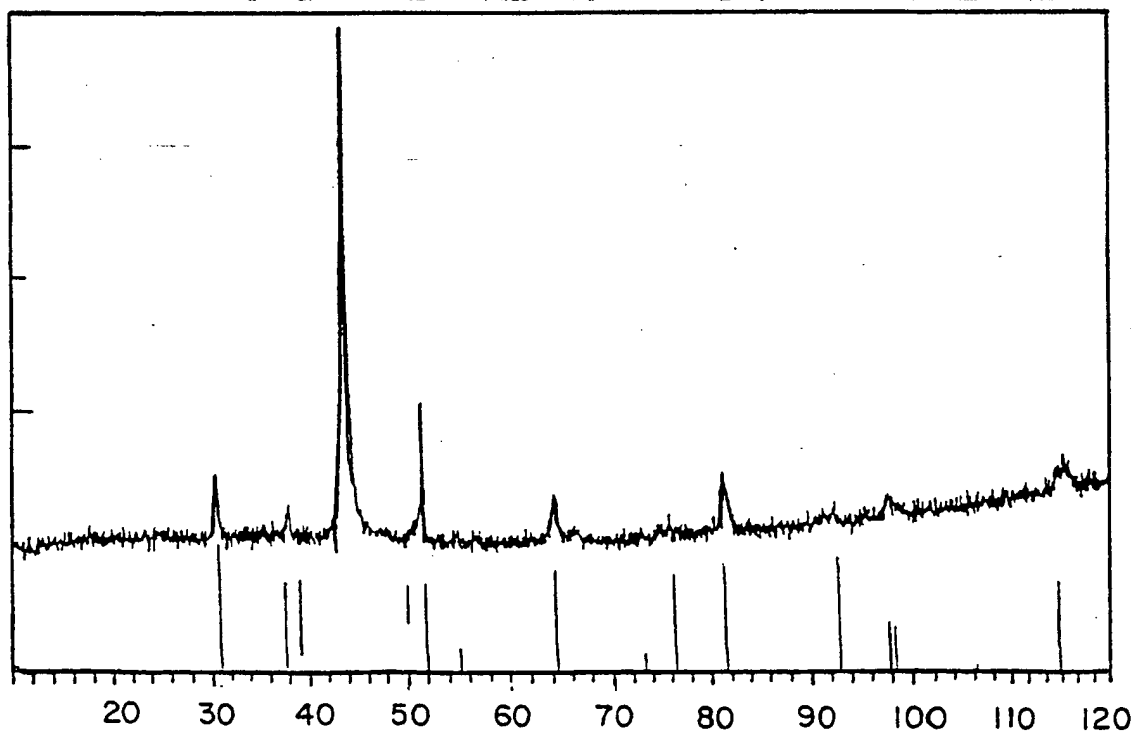


FIG. 12

SUBSTITUTE SHEET (RULE 26)

14/28

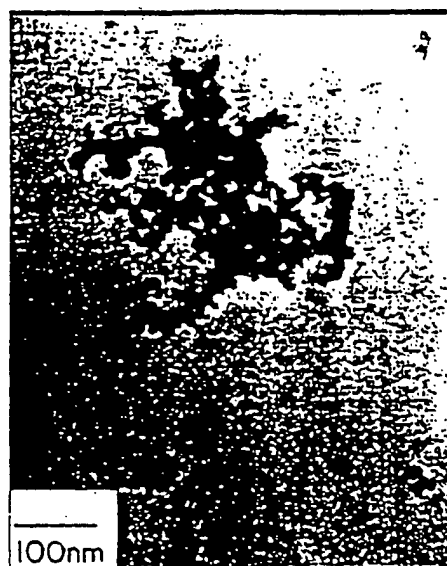


FIG. 13

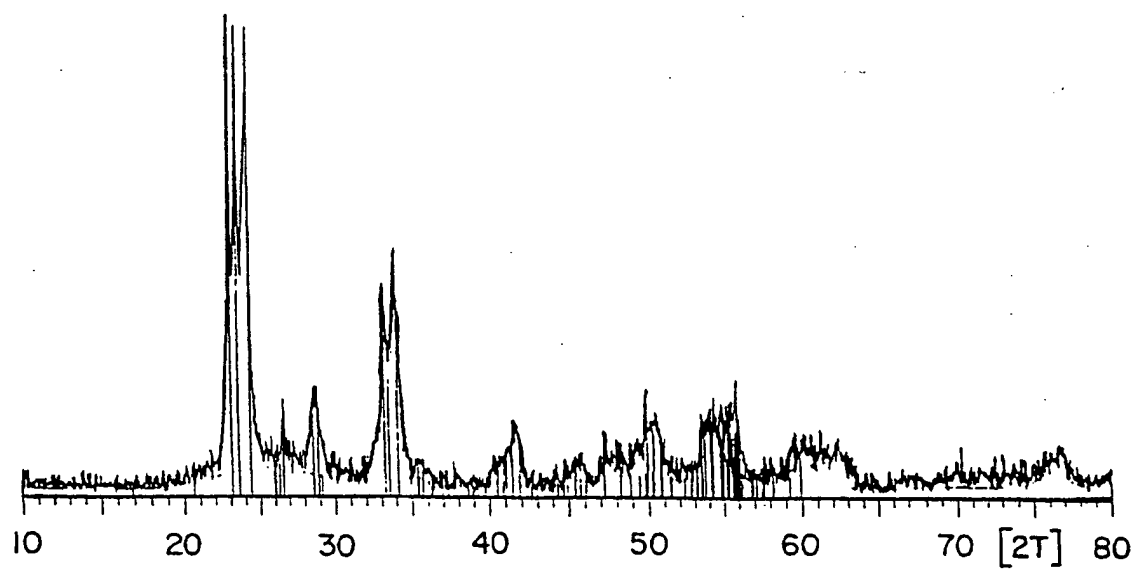


FIG. 14

SUBSTITUTE SHEET (RULE 26)

15/28



FIG. 15

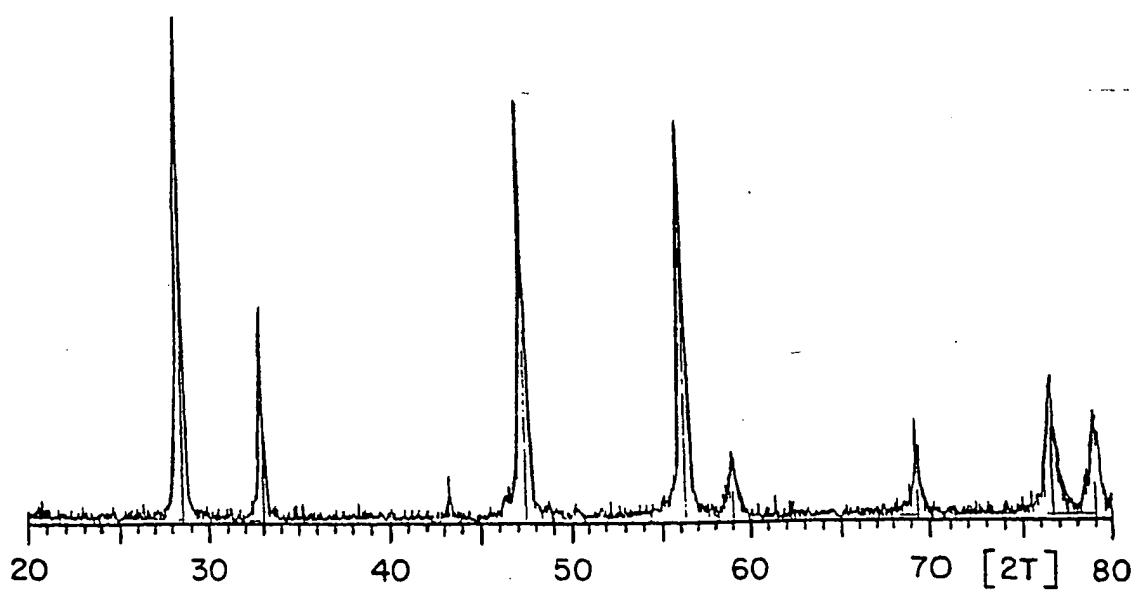


FIG. 16

SUBSTITUTE SHEET (RULE 26)

16/28

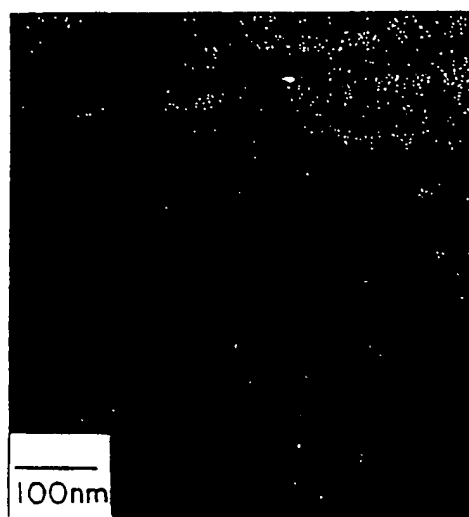


FIG. 17

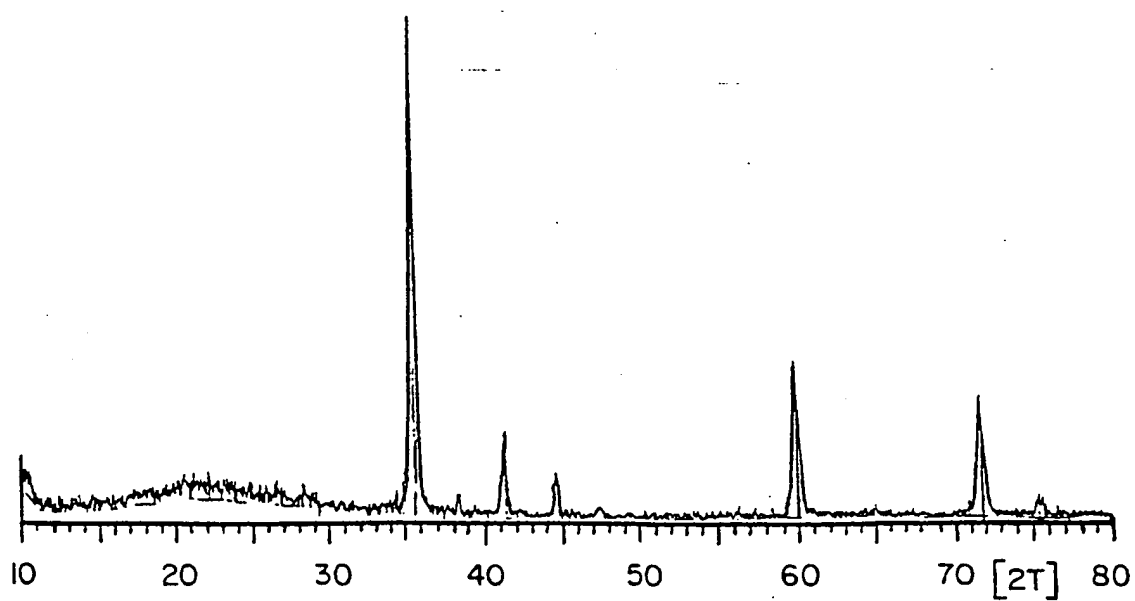


FIG. 18

SUBSTITUTE SHEET (RULE 26)

17/28

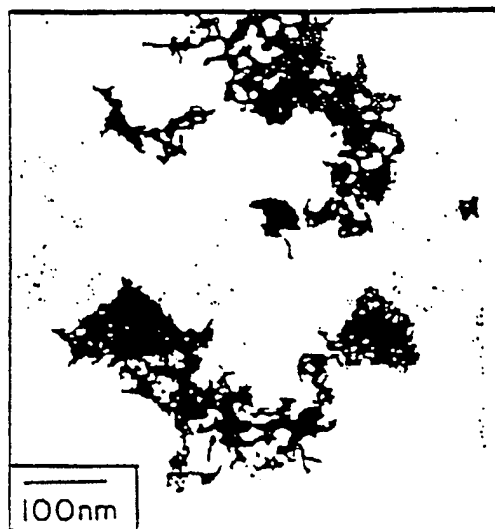


FIG. 19

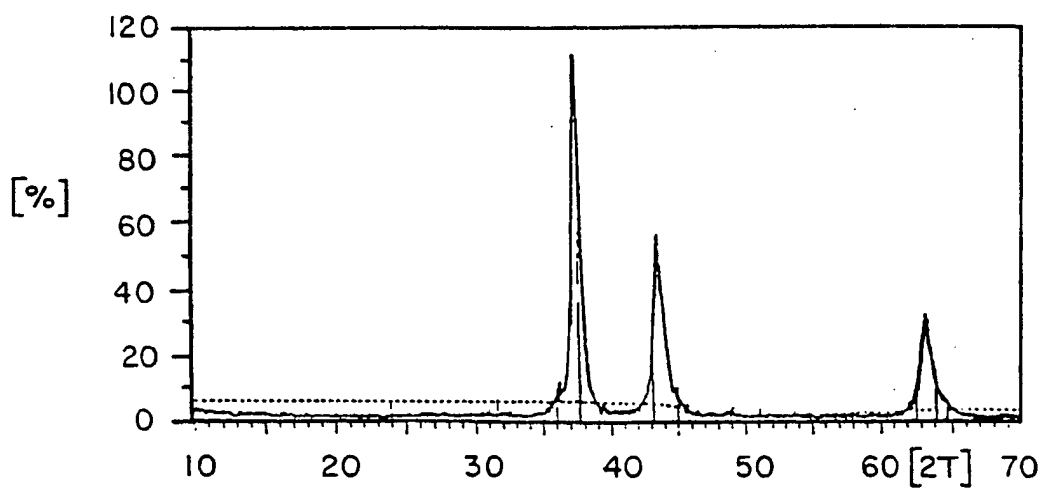


FIG. 20

SUBSTITUTE SHEET (RULE 26)



FIG. 21

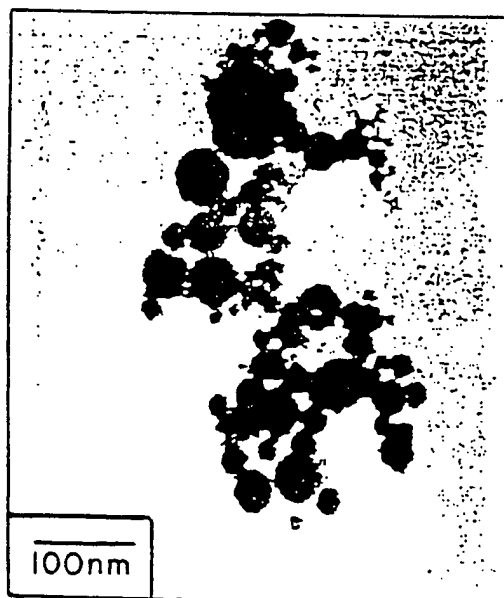


FIG. 26a

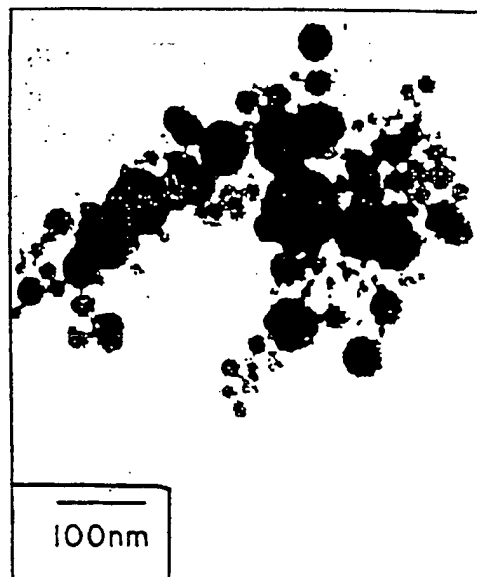


FIG. 26b

19/28

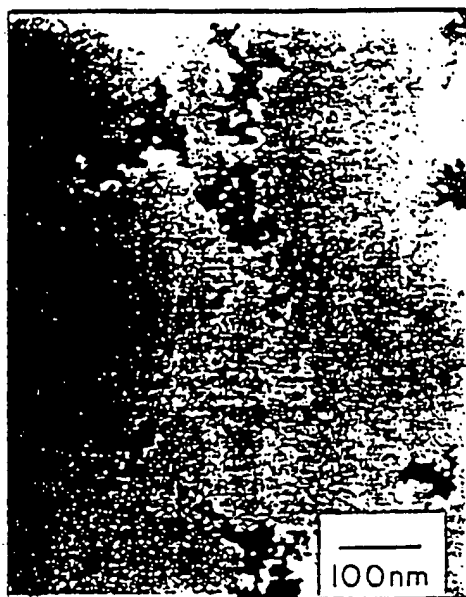


FIG. 22

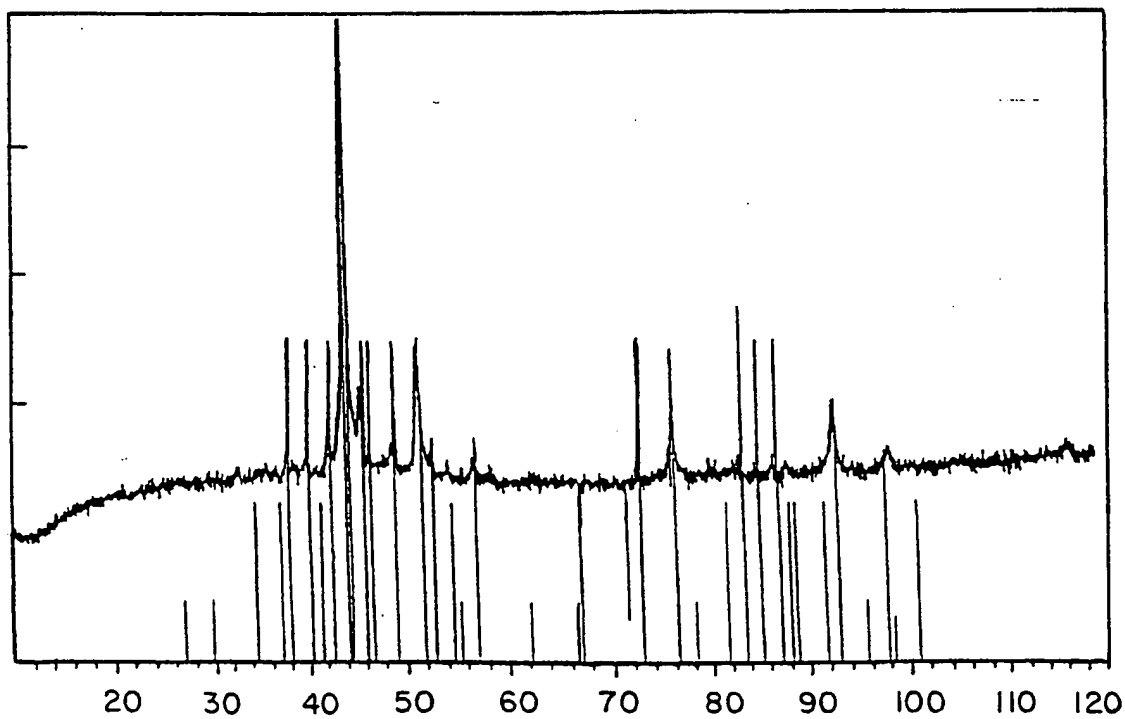


FIG. 23

SUBSTITUTE SHEET (RULE 26)

20/28



FIG. 24

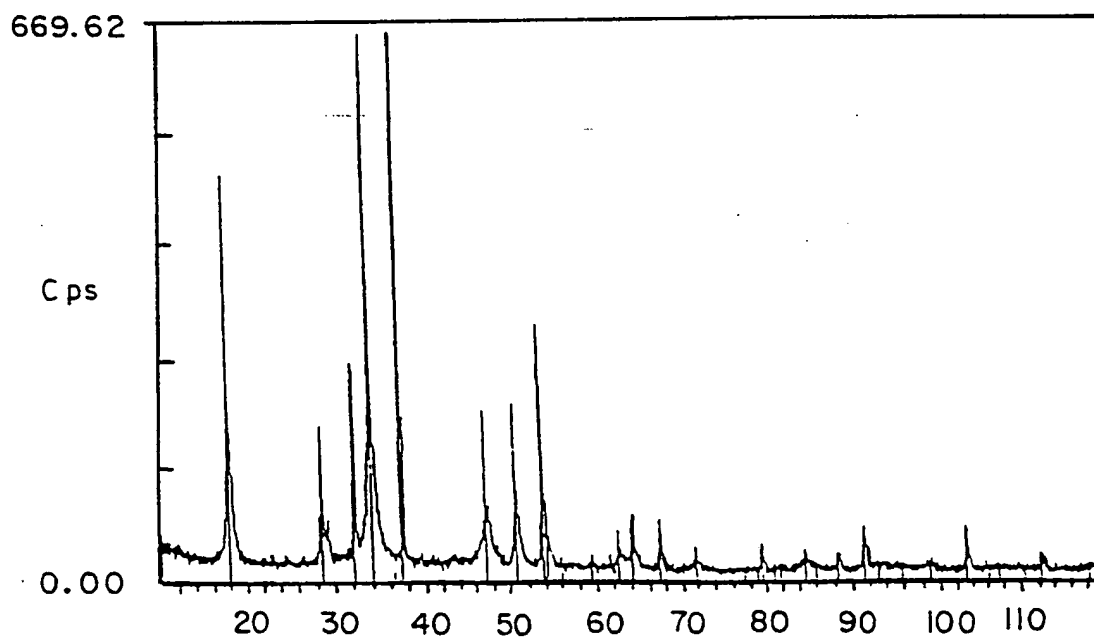


FIG. 25

SUBSTITUTE SHEET (RULE 26)

21/28

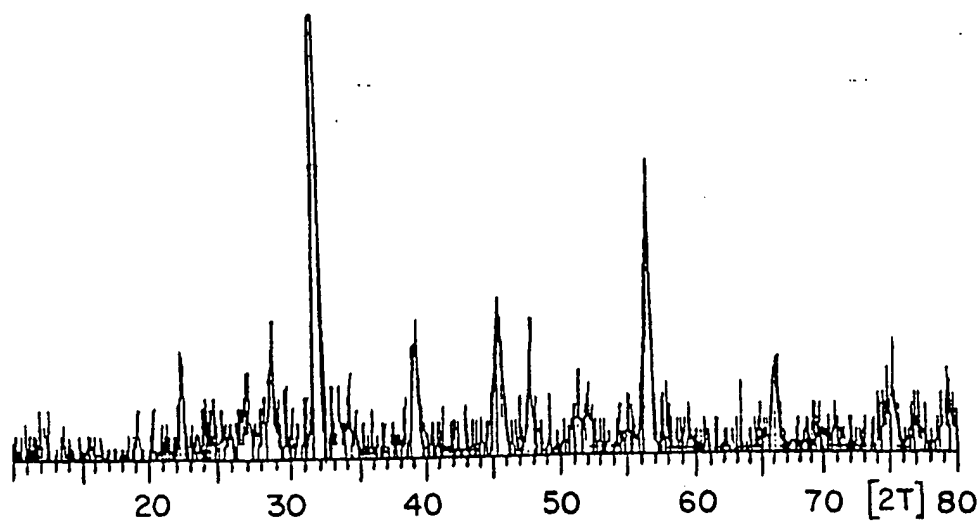


FIG. 27

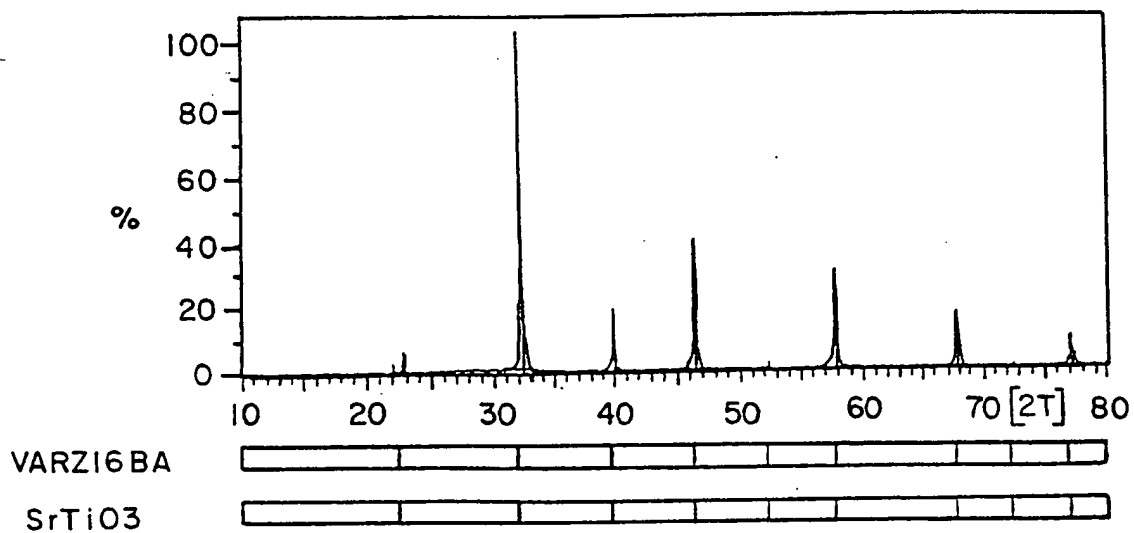


FIG. 29

SUBSTITUTE SHEET (RULE 26)

22/28

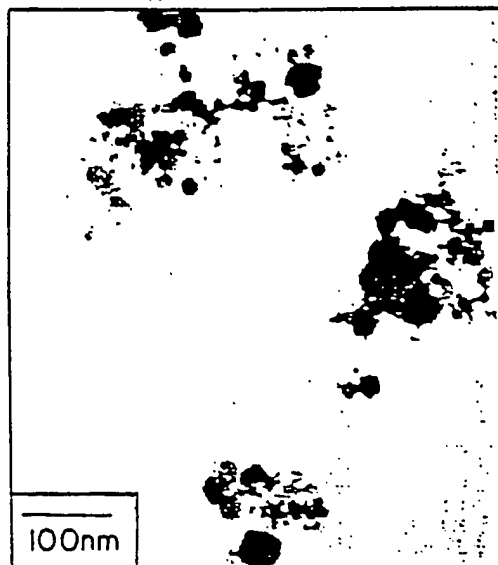


FIG.28a

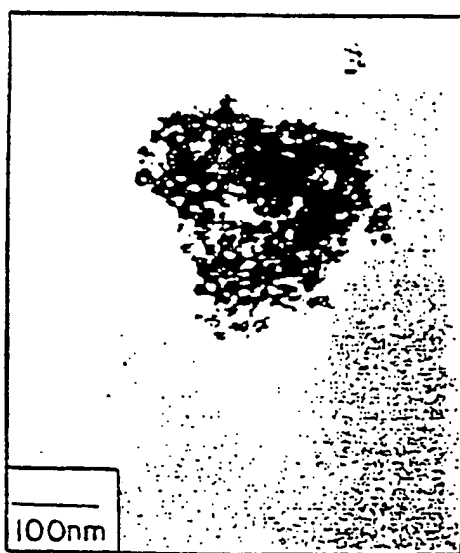


FIG.28b

SUBSTITUTE SHEET (RULE 26)

23/28

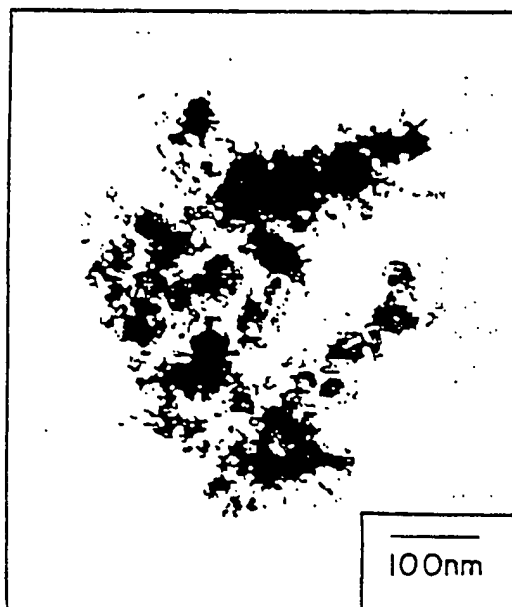


FIG. 30a

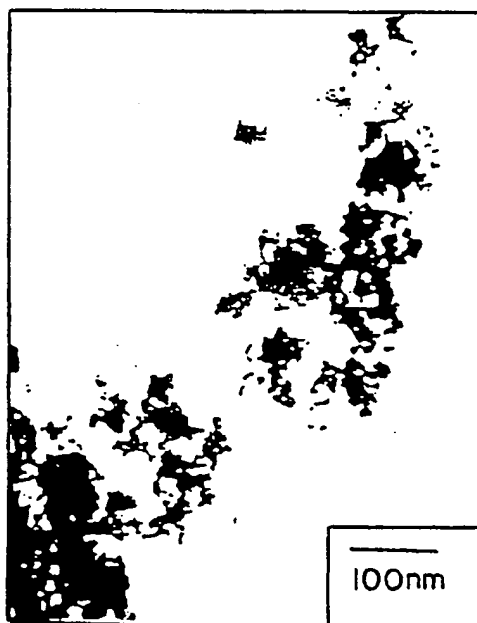


FIG. 30b

SUBSTITUTE SHEET (RULE 26)

24/28

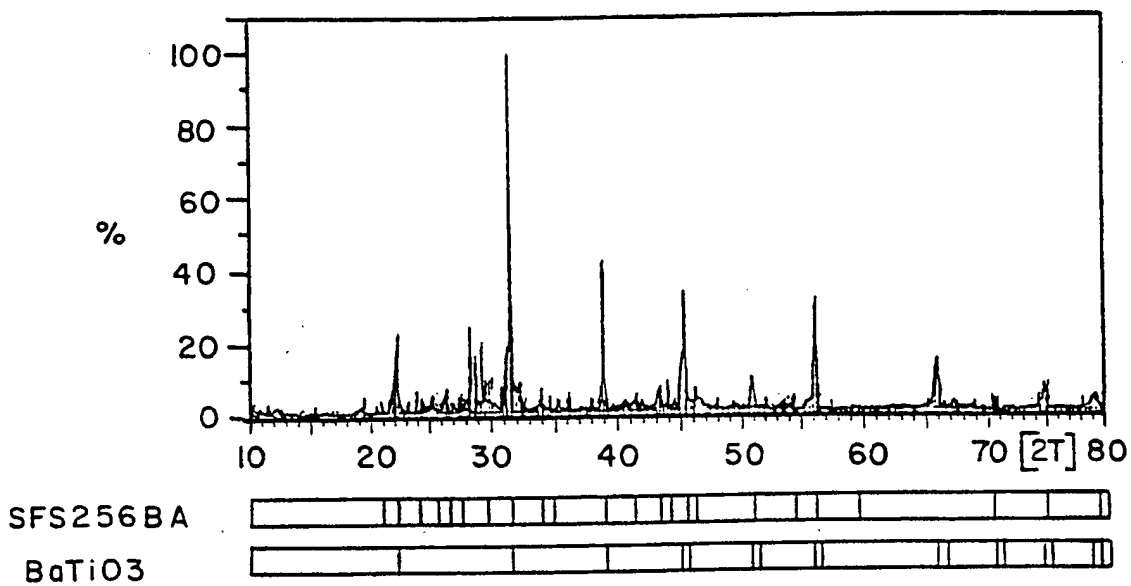


FIG. 31

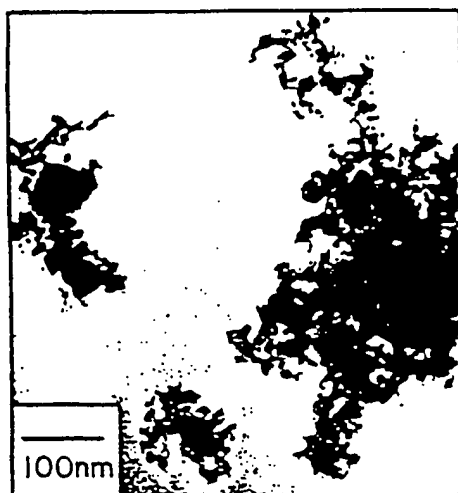


FIG. 32

SUBSTITUTE SHEET (RULE 26)

25/28

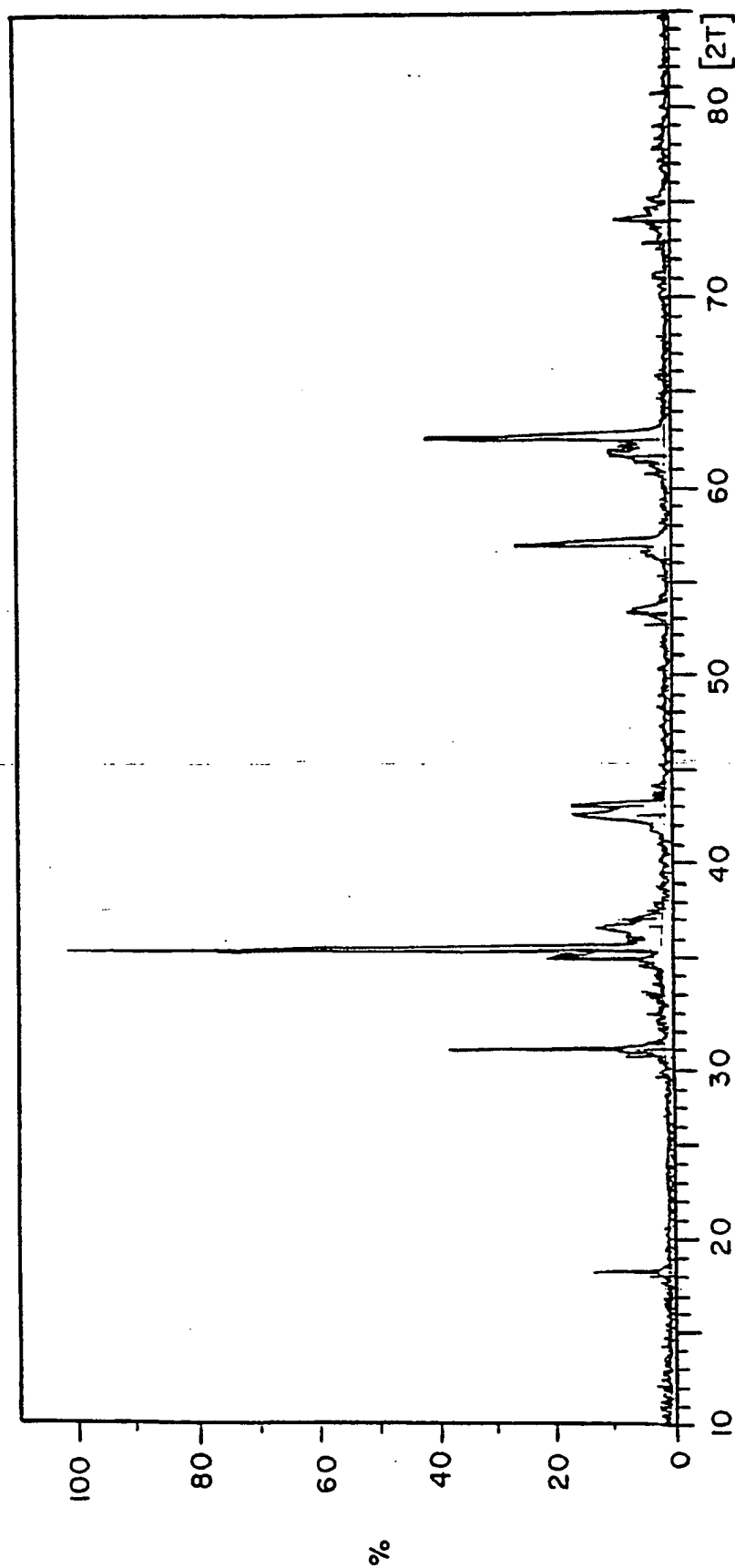


FIG. 33

SUBSTITUTE SHEET (RULE 26)

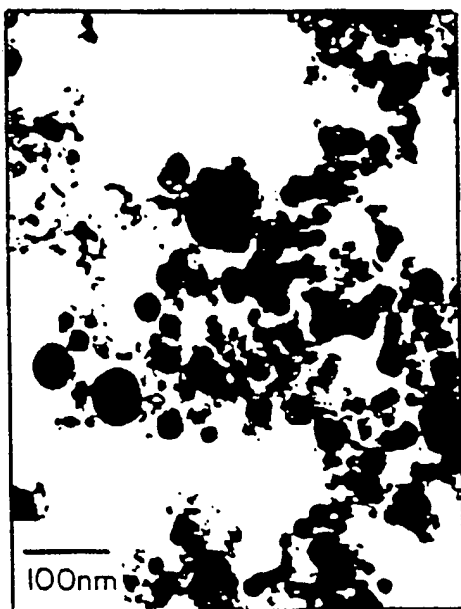


FIG. 34a

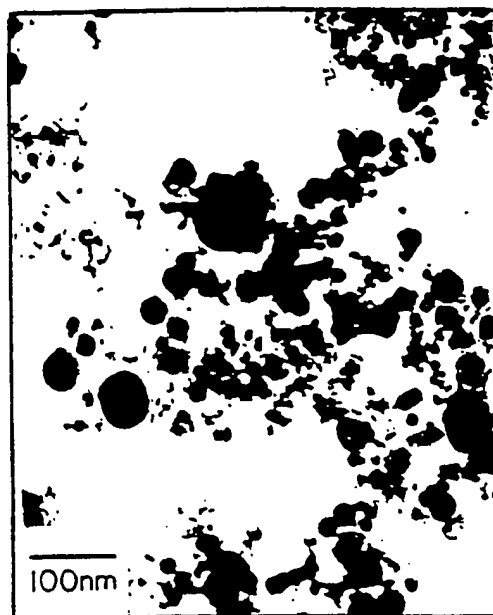


FIG. 34b



FIG. 36

27/28

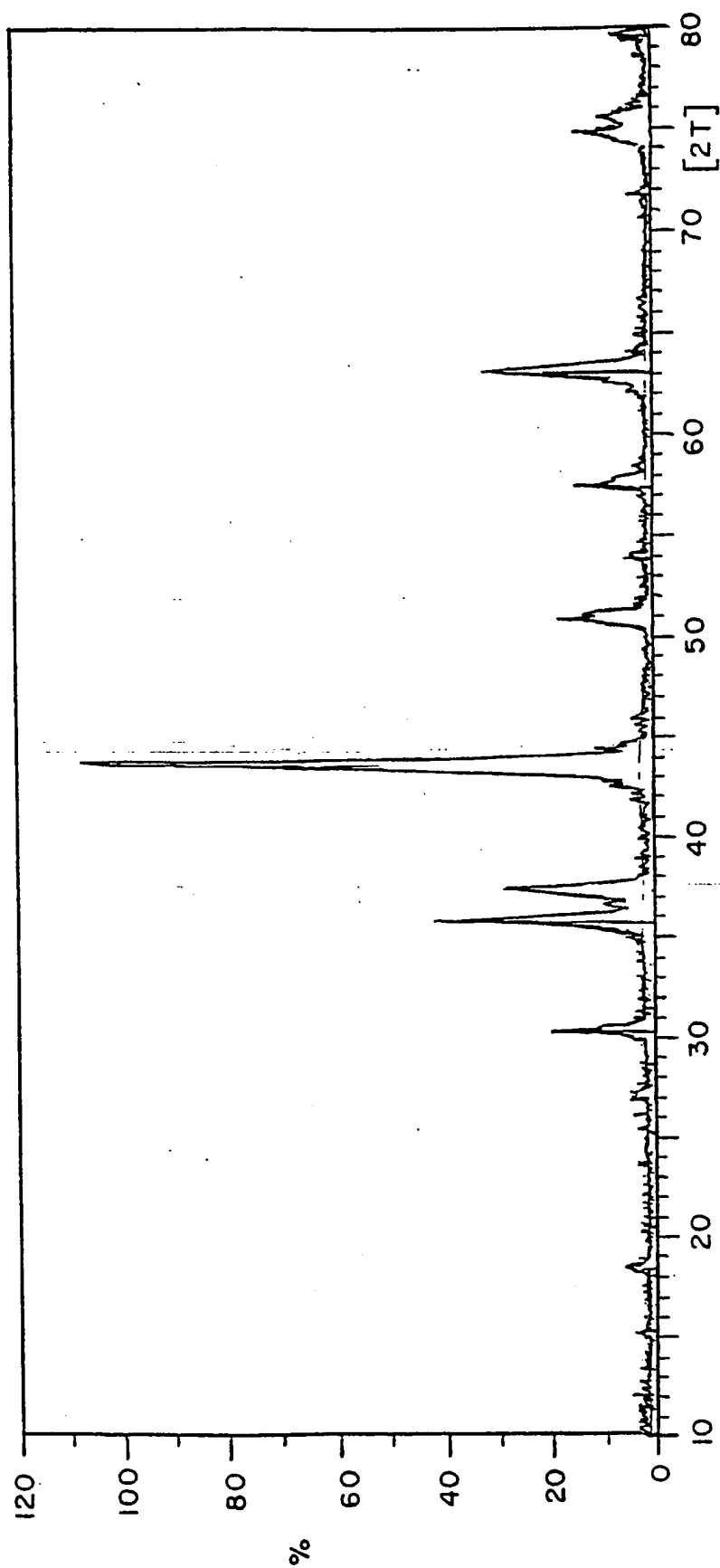


FIG. 35

SUBSTITUTE SHEET (RULE 26)

28 / 28

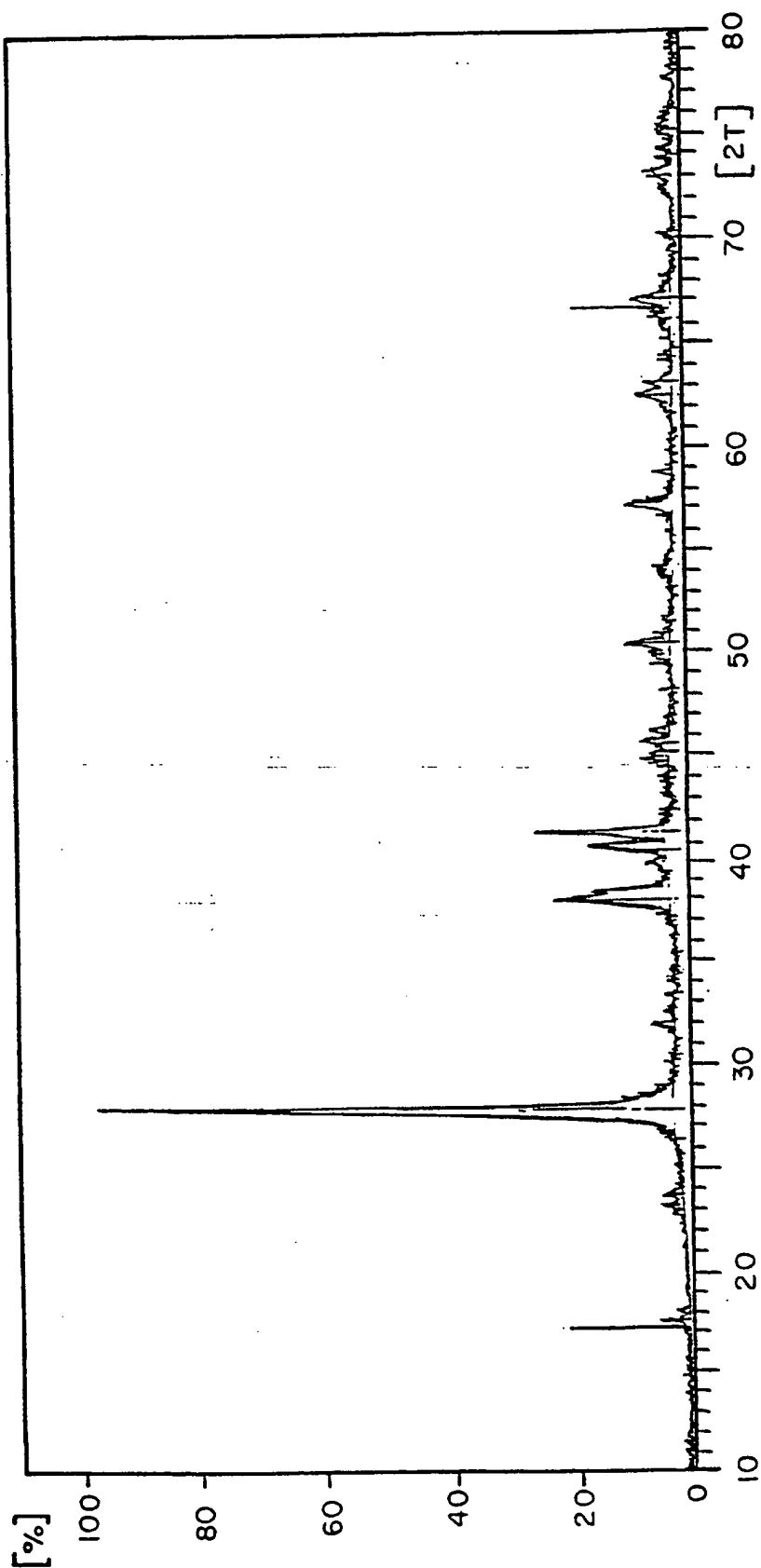


FIG. 37

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/15463

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B22F9/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 851 262 A (MCFEATERS JOHN S) 25 July 1989 -- see whole document -- --/--	1-4, 6-8, 10-19, 22-42, 45, 46, 49, 50, 53-55, 58-60, 71, 72



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

28 January 1998

Date of mailing of the international search report

04/02/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Riba Vilanova, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/15463

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 484 943 A (MIURA HIROHISA ET AL) 27 November 1984 see whole document ---	1,2,4, 6-8,10, 11, 13-23, 25-46, 49,50, 53-55, 58-60, 71,72
X	US 4 892 579 A (HAZELTON LOWELL E) 9 January 1990 see whole document ---	1-23, 25-44
A	US 4 147 534 A (HORI FUMIO) 3 April 1979 see figures see column 3, line 11 - column 9, line 6 ---	1-73
A	GIRARDIN D ET AL: "ULTRAFINE METALLIC POWDERS PREPARED BY HIGH PRESSURE PLASMA: SYNTHESIS AND CHARACTERIZATION" MATERIALS RESEARCH BULLETIN, vol. 25, no. 1, 1 January 1990, pages 119-127, XP000134452 see page 119, line 1 - page 121, line 52 -----	1,4,5, 29,39, 45,46, 49,71

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. onal Application No

PCT/US 97/15463

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4851262 A	25-07-89	AU 590135 B AU 8185287 A	26-10-89 01-12-88
US 4484943 A	27-11-84	JP 1027773 B JP 1543887 C JP 58150427 A JP 1639083 C JP 2055481 B JP 58153532 A JP 1482551 C JP 58153533 A JP 63030963 B EP 0087798 A	30-05-89 15-02-90 07-09-83 31-01-92 27-11-90 12-09-83 27-02-89 12-09-83 21-06-88 07-09-83
US 4892579 A	09-01-90	NONE	
US 4147534 A	03-04-79	JP 1073040 C JP 53022810 A JP 56015697 B AU 503218 B AU 2794077 A CA 1090142 A DE 2736806 A FR 2362214 A GB 1558109 A US 4200264 A	30-11-81 02-03-78 11-04-81 30-08-79 22-02-79 25-11-80 23-02-78 17-03-78 19-12-79 29-04-80

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.